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HISTORY OF CHEMISTRY

Lectures on the History of the Development of Chemistry since the Time of Lavoisier

BY DR A. LADENBURG
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TRANSLATED FROM THE SECOND GERMAN EDITION

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With additions and corrections by the Author

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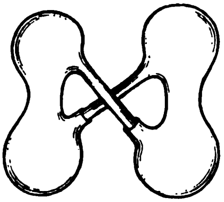

AUTHOR'S PREFACE

In placing these lectures before a wider section of the public, I consider it essential to indicate the point of view from which they have been prepared. I regard them as an attempt to follow the development of our ideas of to-day from those that were formerly current. Hence I have only gone back as far as Lavoisier; because our science assumed a new aspect in his hands, and because it may be held that, as regards development, we are still passing through the epoch inaugurated by him.

It has been my wish to arrange the matter of the lectures in such a way that the student may be enabled to obtain a survey of this portion of the history of chemistry with little trouble, and at the same time so that it may serve as a guide for those who may desire to engage their attention more particularly with special investigations in this department. On this account I have expressed myself as concisely as possible, whilst, on the other hand, I have supplied moderately complete references to the original literature in connection with the subjects treated of. A twofold result appears to me to be attained in this way, inasmuch as the reader is placed in the position of being able to form an opinion forthwith regarding the value of the narrative, and to correct errors and omissions, while the labour of subsequent investigators is lightened. While I could scarcely consider it possible to give an absolutely accurate representation of the period in question, with its great wealth of discovery, still it has been my aim to furnish a useful contribution towards the history of the chief chemical facts and theories.

It is almost unnecessary to say that the book has no pretentions to completeness. I only felt justified in taking notice of those investigations and ideas which have exercised an influence upon the further development of chemistry, whereas I have at most merely referred to other investigations which, in my opinion, will still exert such influence. An objective treatment of the subject appeared to demand that it should be handled in this way.

I have not hesitated to carry the history of the development of chemistry down to the present day, although the difficulty of the task has been greatly increased by my doing so. It is certainly in this part in particular that many corrections will still be necessary before the end in view is attained. How different the latest phases of our science will appear to subsequent investigators! And yet the opinion of a contemporary is not without value also, when it is moderate and free from prejudices or special leanings. This is exactly what I have striven to attain. If I have not always been successful in doing so—if here and there I may have underestimated the merits of some and unduly asserted those of others—this has been unintentional. If I have been severe in my judgment, I have at least been free from any personal feeling, and it has always been the matter alone that I have attacked. Should I have approached in some cases too closely to the limits of historical accuracy, or should I not have succeeded in representing fairly the claims of every one, I am fully prepared to rectify my error as soon as I am convinced of it.

If my colleagues are interested in the subject, and assist me with their knowledge and advice, it may soon be possible, perhaps, to obtain an objective picture of the chemical theories of the last hundred years. I desire that this book may be regarded as an attempt in that direction, and that it may be judged indulgently.

A. LADENBURG.

KIEL, *December* 1886.

AUTHOR'S PREFACE TO THE ENGLISH EDITION

THIRTY years after the appearance of the first edition of this book, an English translation of it is now being prepared. I regard this as a favourable indication of the permanent value of the book, since it is evident that the standpoint then adopted is intelligible at the present day and is still unsuperseded. Moreover, it may be concluded that the exposition of the subject is not marred by national prejudices.

In order to keep pace with the constant progress of the science, two new lectures have been added to the original fourteen. One of these appeared fourteen years ago, upon the publication of the second German edition of the book; whilst the other—the sixteenth—is here published for the first time.

The English edition is a faithful translation, and so far as I am able to judge, it is written in a good style. For these features my best thanks are due to the translator.

I venture to express the hope that the book will find friends amongst the English-speaking peoples, and that it may contribute to stimulate interest in the history of our science.

A. LADENBURG.

GRASSENDALE, SOUTHBOURNE-ON-SEA,
September 1899.

TRANSLATOR'S NOTE

THE translator wishes to express his sincere thanks to Professor Ladenburg for the very cordial manner in which he agreed to the preparation of this translation of his well-known history, as well as for his kindness in specially writing an additional lecture for the English edition, thereby bringing the latter up to date; also for the great care he bestowed upon the revision of the proof-sheets. He further wishes to thank a number of friends to whom he is indebted for advice and assistance upon a variety of points.

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NOTES RESPECTING THE REFERENCES TO JOURNALS, ETC.

IT is not anticipated that the abbreviations employed for the titles of journals, etc., will, as a rule, present any difficulty. The following unfamiliar abbreviations may be explained:—

A. C. R. = Alembic Club Reprints.

E. (following a reference to a foreign book) = English Translation. (This contraction is only employed in the cases of a few well-known translations.)

In cases where journals have been issued in two or more series, references to volumes belonging to the second or any subsequent series have the series indicated by prefixed numerals enclosed within square brackets.

HISTORY OF CHEMISTRY.

LECTURE I.

INTRODUCTION—THE PHLOGISTON THEORY IN ITS FIRST AND IN ITS LATER ACCEPTATIONS—CHEMICAL KNOWLEDGE OF THE PHLOGISTIANS—FALL OF THE SYSTEM.

THE value of historical narratives is undisputed. This value no doubt varies with the subject matter which is dealt with ; but the history of human actions and of human knowledge always forms one of the most interesting inquiries. If we are adherents of the Darwinian theory, and grant to this theory a warrantable latitude, the importance of a retrospect of bygone centuries is thereby enhanced. We are then obliged to recognise a steady progress of development ; history is no longer a mere enumeration of isolated facts in chronological order, as these succeeded one another fortuitously, but it embraces the development of the human mind and of human civilisation. It shows us the results of the influence which the most varied causes have exercised upon the most different natures, and may perhaps at some time enable us to discover the laws which regulate these results. From this point of view it cannot be denied that the development of the present condition out of any former one becomes of increased importance ; and hence the interest which the thinking public has taken in Buckle's "History of Civilisation" is easily understood.

I do not, however, go so far as to assert that this actual standpoint is necessary in order to lend due importance to the representation of the past. The facts cannot be overlooked, that knowledge itself affords a certain satisfaction to the human intellect, and that every one eventually seeks to draw lessons for the present from the destinies of nations in former times. The most pronounced opponents of Darwin, for example, must admit that a connection exists between the predominating character and the fate of a nation, and even they will attribute the success or the non-success of great undertakings to material causes and circumstances.

Assuming as a basis, then, the standpoint mentioned above, it may be asserted that a historical account of any science possesses an interest extending beyond that particular science. In a comparative study of the history of all intellectual sciences, certain general tendencies of speculation may perhaps be recognised which were predominant at particular times, and owed their existence to real, definite circumstances. In this respect the history of philosophy, in particular, is of importance for early times; while for modern times the historical exposition of the natural sciences, in my opinion, possesses just as great, and probably even greater, importance. The subject matter treated of in the present work may hence find an application some day: it may be regarded as one of the many preparatory studies which will be required if the question of writing a history of the development of the human intellect should ever arise.

If we limit our view, however, and inquire as to the interest which the historical representation of a science possesses for that science; or, what concerns ourselves still more closely, if we merely consider the advantage which accrues from it for the study itself, or for the student, the points of view which then become paramount are entirely different.

A retrospect of the past, especially in the exact sciences, alone affords a proper comprehension of what is accepted to-day. It is only when we are acquainted with the theories which preceded those accepted at present, that the latter can be fully understood; because there is almost always an intimate connection between them. It might appear in our science (where any final result is arrived at by the test of experiment) that the earlier views, which give expression to a limited number of facts only, must not merely be supplanted by the later theories, which deal with a larger class of phenomena, but that they must lose their importance altogether. For the most part, however, this is not the case. On the contrary, a certain connection between successive hypotheses can very frequently be observed. When the general development is followed up, the effects of the earlier ideas can be recognised in the later views, and it is in this way that the latter first come to be properly understood. The abandonment of a theory is not always accompanied by a revolution. Such, indeed, is scarcely conceivable in the higher stages of the development of science; and even when new modes of explanation are proposed, traces of former opinions may still be recognised in the direction which these take.

But quite apart from this real advantage of the study of history, which thus, in my opinion, leads to a clearer understanding of our present position, yet another advantage may be adduced which is perhaps of still greater value to the student: namely, the accurate estimation of the value of theories. An examination of the past shows us the mutability of opinions; it enables us to recognise how hypotheses, apparently the most securely established, must in course of time be abandoned. It leads us to the conviction that we live in a state of continuous transition; that our ideas of to-day are merely the precursors of others; and that even they cannot, for any length of time, satisfy the requirements of science. We learn from any historical exposition that our natural laws are not incontrovertible truths or revelations, but that they can be regarded as the expression, for the time being, of a certain series of facts, which are thereby summarised and, as we say, explained in the most practical way for us. We recognise that these laws do not originate suddenly in the head of a single individual, like Minerva in the head of Jupiter. It is only slowly that the fundamental ideas which underlie them mature, and that the requisite facts are ascertained by the labours of many; until, at last, the law common to them all is announced by some one, or often by several persons simultaneously. Further, by the study of history our faith in authority is diminished—a faith which produces pernicious effects by obstructing the way for any original development of the individual.

On the other hand we also learn, it is true, that theories are necessary for further development; and that, although the actual teachings of science may lie in the facts, the real intellectual significance can only be acquired by connecting isolated observations by means of hypotheses; so that the present position consists far more in the mode of explaining observations than in the observations themselves.

When the point of view which I regard as essential for our subject is thus made clear, it will be understood that I direct my attention principally to theories, and only take cognisance of those experimental investigations which have contributed to the establishment or the overthrow of general views.

The early history of our science has been treated most excellently, and in detail, by Hermann Kopp; and for this reason I confine myself to the period since the time of Lavoisier; that is, to the period of modern chemistry, or to that of quantitative investigations.[1] I must not omit, however, to give a short description of the views which prevailed in chemistry prior to Lavoisier.

The influence of the Greeks upon art and literature, on their reawakening after several hundred years' sleep, is so well known that it need not surprise us if we recognise a similar influence in science also. The four elements of Empedocles, water, earth, fire, and air, which, in Aristotle's system, are representative of the four cardinal properties, moist, dry, hot, and cold, are quite familiar. I attach great importance to finding fire here amongst the elements, and to seeing it regarded as a material substance. As we shall learn in what follows, the first chemical theories have reference to the phenomena of combustion, and the phlogiston theory becomes more comprehensible when we minutely study the views of the Greeks and the Romans. Amongst these peoples, combustion is already looked upon as consisting in the separation of the material of fire; and Pliny regarded the easy inflammability of sulphur as a proof of its being largely composed of a fire material.[2] At a later date sulphur was itself assumed to be the fire material; and from that view the hypothesis that all metals contained sulphur, unquestionably arose.

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[1] Kopp's Entwickelung der Chemie in der neueren Zeit (1873) appeared five years after the publication of the first German edition of this book.

These few words concerning the chemical theories of the ancients appear to me sufficient in order to understand Becher and his follower, Stahl. Both of these based their views upon those of the Greek and of the Roman philosophers; in the same way that we find so many imitators of Greek art at the same period, that is, in the seventeenth century.

A difference may, it is true, be pointed out between them; namely, that only the latter intentionally and knowingly followed in the footsteps of the ancients, whilst the former declared themselves to be their opponents. Thus Becher says: "A good peripatetic is a bad chemist." He replaces the four elements of Empedocles by three others: the vitrifiable, the inflammable, and the mercurial earths.[3]

It is not my business here to inquire whether it was Becher or Stahl who thought and wrought most with respect to the phlogiston theory. Still I will not omit to draw attention to the great modesty of Stahl, who wished that his own services should be attributed to his teacher and friend Becher: "*Becheriana sunt quae profero.*"[4] Such examples are rare.

The adherents of the phlogiston theory regard combustion as consisting in a decomposition: "only compound substances can burn"; these all contain a common principle which Becher calls *terra pinguis* and Stahl calls Phlogiston. During the combustion this principle escapes and the other constituent of the substance remains behind.

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[2] Kopp, Geschichte. 3, 102.

[3] Ibid. 1, 179.

[4] Ibid. 1, 188.

This theory was applied to all combustible substances. Thus, according to Stahl's views, sulphur consists of sulphuric acid and phlogiston ; a metal, of its metallic calx (of its oxide we should say) and phlogiston. According to Stahl, sulphur was not identical with phlogiston, but, as with Pliny, it was rich in the principle of inflammability, which he did not know in a separate state. Soot appeared to be the substance richest in phlogiston ; in fact as almost pure phlogiston. It was in consequence of this that the conversion of the metallic calx into the metal by heating it with soot succeeded so well ; for the soot handed over its phlogiston to the metallic calx, so that a metal was produced again. In his *experimentum novum* Stahl tries to prove that the phlogiston in soot and in sulphur is identical. He shows here, how a sulphate can be converted by means of charcoal into liver of sulphur, from which sulphur is precipitated by the action of an acid. From the reduction of the metallic calces by means of soot, Stahl further infers the identity of the phlogiston of the metals with the inflammable principle in soot and in sulphur ; and thus he arrives at a proof that there exists only one such principle, which he calls simply Phlogiston (from φλογιστός, combustible).

The phlogiston theory was, for a century, the basis of all chemical considerations ; nevertheless we shall find that during this time the conception of phlogiston did not always retain its first signification, and that the whole mode of regarding it was altered in consequence.

We can understand Stahl and his immediate followers quite well if we assume a loss of oxygen in every place where they speak of the taking up of phlogiston, and *vice versa;* a phlogisticated substance is, with us, a substance free from or poor in oxygen. It might perhaps be said, in short, that phlogiston is negative oxygen.

Stahl borrowed from the ancients the view that combustion is accompanied by destruction, or decomposition. This he retained, although, even in his time, facts were well known which proved an increase of weight on combustion. Even Geber, an alchemist of the eighth century, appears to have observed this in the cases of tin and of lead; and the chemical literature up to Stahl's time furnishes several statements of the same kind. Highly interesting, for example, are the observations of Jean Rey, of Mayow, and of Hooke, as well as the conclusions which they drew from them. I shall enter into these in the next lecture.

Can we avoid being astonished when we read that Becher and Stahl knew of these experiments and still defended their views; that they regarded the increase of weight merely as an incidental, unimportant phenomenon; and that either the authority of the ancients, or the phenomenon of combustion itself, which with them was so intimately associated with the idea of destruction, was a sufficient ground for neglecting facts which must otherwise have overthrown their edifice? It is more particularly noteworthy, however, that Boyle—one of the most considerable thinkers of the seventeenth century, a predecessor of Stahl, calling himself a follower of the Baconian school; who was aware, from his own experiments, of the increase of weight on combustion; who knew that the air was necessary for this, and who had made the observation that during combustion a part of the air is absorbed—could not make up his mind whether sulphuric acid was a constituent of sulphur, or on the other hand whether sulphur was contained in sulphuric acid.[5]

Amongst the successors of Stahl we find, it is true, some who direct their attention more fully to this increase of weight. Lemery, for example, towards the end of the seventeenth century, states his views about it at length.[6] At the same time his belief in the existence of phlogiston remains unshaken, although combustion now becomes a sort of double phenomenon. It remains a decomposition; that is, the burning substance separates from its phlogiston, but simultaneously it unites with a ponderable fire material. Lemery obtained his ponderable fire material from the same source as that from which Becher had taken his *terra pinguis* and Stahl his phlogiston. It was a new application of the element fire. This double principle—the combustible principle on one hand, the ponderable fire material on the other—satisfactorily and completely explained the phenomena of combustion to the chemists at the close of the seventeenth century. We find these views first shaken by Newton, for whom fire is not a special substance. He suggests that every strongly heated and glowing substance burns; that red-hot iron or wood may be called fire; and that those substances which emit much smoke burn with a flame.

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[5] Kopp, Geschichte. I, 166.

[6] Ibid. 3, 123.

The assumption of this ponderable fire material was first recognised as really fallacious in consequence of a highly interesting experiment by Boerhaave, who weighed masses of metal both cold and red-hot and found their weights to be identical in both cases.[7] The explanation of the increase of weight next brings about differences of views amongst the chemists of the eighteenth century. Some seek to regard it, as Stahl had done, as an unimportant phenomenon which may be neglected; others, on the contrary, and amongst them Boerhaave, assume a union with certain (saline) portions of the air, and in this way seek to take account, at the same time, of the necessary presence of air during the combustion and of the increase in weight. According to others again the air merely serves to take up the separated phlogiston, which, in their view, cannot escape from one substance if there is not another present with which it can unite. In the middle of the eighteenth century we also find the notion that phlogiston possesses negative weight, or absolute levity. It seems quite natural to the upholders of this hypothesis that the weight increases on the separation of phlogiston. Others still, who have difficulty with the conception of absolute levity, regard phlogiston as lighter than air. This view is upheld, for example, by Guyton de Morveau,[8] whose explanation of the increase of weight is based upon the Archimedean principle, and does not altogether tell in favour of the clearness of imagination of this noted chemist. He says in effect:[9] If we bring two lead balls of approximately equal weight into equilibrium under water, on a balance, and then attach a piece of cork (an object lighter than water) to one of the balls, this ball will ascend; it becomes, therefore, apparently lighter although clearly we have increased the weight. A similar thing holds in combustion; in this case we weigh in air; the metal—the compound of the metallic calx with phlogiston—appears to be lighter than the calx because the phlogiston, just like the cork, is specifically lighter than the medium in which we weigh.—I take it for granted that the reader perceives the fallacy in this mode of regarding the matter; and in this respect he is in advance of the celebrated Macquer who could not withhold his admiration for this explanation.—Even Boyle had already observed that the metallic calces were specifically lighter than the metals, but Guyton does not take this into consideration!

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[7] Kopp, Geschichte. 3, 127.

[8] Ibid. 3, 149.

As the reader will have observed, I have not hesitated to call attention to the contradictions of the phlogiston theory, and to its weakness with respect to any reasonably tenable explanation of the increase of weight during combustion. In spite, however, of those hazy conceptions, which constituted the basis of the chemical opinions of the period, there were men amongst the phlogistians who have scarcely been excelled in the fertility of their discoveries by any of the chemists of the present day. In this connection may I venture to make a general statement? Am I not justified in asserting that fallacious theories are not always obstructive to the development of science, and in supporting the view that it is better to possess definite theoretical bases, even if they do not explain all the facts, than to represent these facts themselves as the sole triumphs of science? Facts certainly play a great part in the foundation and in the overthrow of a theory; indeed they alone should have any influence in such matters; and if we now turn our attention to the decline of the phlogiston theory, we must consider, in a general way at least, the chemical knowledge and labours of the phlogistians.

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[9] Kopp, Geschichte. 3, 149.

Their chemistry consisted especially of a rather incomplete knowledge of the chemical and physical properties of a series of substances which occur in nature. They had learned how to prepare other substances from these, and their endeavours were directed to the discovery and recognition of new substances. Hence we find an already remarkable development of qualitative analysis, which we owe chiefly to Bergman, whilst quantitative methods were almost wholly unknown. Naturally, the theoretical bases did not permit of any value being attached to chemical proportions by weight.

In order to give a general idea of the substances known at that time, I shall mention some of them. Sulphur, charcoal, gold, silver, copper, iron, tin, and lead were certainly known to the most ancient peoples; the discovery of mercury belongs to the Greek period; that of antimony, bismuth, and zinc to the middle ages; that of arsenic, phosphorus, cobalt, nickel, platinum, etc., to the period of phlogiston. Scheele, who was the most fertile discoverer amongst the phlogistians, discovered manganese and chlorine. The metallic calces, or oxides, as we should say, were looked upon as different by all the chemists of the period; yet Macquer thought this difference might be referred to the more or less incomplete expulsion of the phlogiston, and he therefore assumed the existence of the same earthy constituent in all the metals.[10] Amongst those earths which were not classed with the metallic calces, they knew lime, alumina, and magnesia. Scheele discovered baryta. They divided the alkalies into the caustic and the mild (carbonated), the latter being regarded as substances which might pass into the former by taking up fire material. Potashes were in use from the earliest times; the Arabians probably made known the preparation of caustic potash from potashes and lime; nitre was also known, and served for the manufacture of gunpowder. Soda or potash had been already employed by the Egyptians in the manufacture of glass,[11] but Stahl was the first to discover that common salt contained an alkali differing from potash.

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[10] Kopp, Geschichte. 3, 143.

Amongst the acids known at that period, I mention hydrochloric, nitric, sulphuric, and acetic. We are indebted to the Arabian alchemists for the introduction of the use of *aqua regia*. Scheele considerably increased the number of the organic acids. He discovered hydrocyanic, malic, uric, lactic, citric, oxalic, and gallic acids. The discovery of hydrofluoric acid also stands to his credit. So we see what a large number of salts the phlogiston period had at its command in consequence of these discoveries. I do not enlarge upon this, but turn to the knowledge respecting the gases, which are all the more interesting because they led to the downfall of the phlogiston theory.

All gases were for a long time regarded as identical with air, and this in turn was considered to be an element. Van Helmont, in the middle of the seventeenth century, was the first who assumed the existence of different gases. Nearly another hundred years passed after this assumption before the recognition of a gas which was certainly different from air ; the difficulties of the manipulation make this easily comprehensible. We are especially indebted to Black, Cavendish, and Priestley for surmounting these difficulties. The first examined carbonic anhydride, or the so-called fixed air, and corrected the views as to mild and caustic alkalies. His investigation [12] is one of the most important of the phlogiston period. In it (as was done by Lavoisier at a later date) we find the relations by weight brought forward as the most important consideration in the arguments. Cavendish studied the properties of hydrogen, whilst Priestley discovered oxygen, nitric oxide, and carbonic oxide, as well as sulphurous and hydrochloric acid gases, ammonia, and silicon fluoride.

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[11] Kopp, Geschichte. 4, 27.

[12] Experiments upon Magnesia Alba, Quicklime, and some other Alcaline Substances. See Alembic Club Reprints, No. 1.

I shall deal more fully in the next lecture with the discovery of oxygen and the theoretical revolution connected with this discovery. I shall now say something with respect to Cavendish's investigation of hydrogen, and shall refer particularly to the modification in the prevailing phlogiston theory, which Cavendish and some other chemists introduced as a result of this investigation.

Cavendish prepared his hydrogen from iron, tin, or zinc by dissolving any of these in hydrochloric acid; he studied its physical properties, called it inflammable air, and proved that it was quite distinct from common air. Basing his opinion on its mode of preparation, he regarded it, in the same way that Lemery had already done,[13] as identical with phlogiston. Priestley and Kirwan further developed this view, the former basing his opinion upon his own observation that the metallic calces were reducible by means of hydrogen.[14]

The phlogiston theory in this new form is really based upon the following views: When a metal is treated with a diluted acid it decomposes into free phlogiston (hydrogen), and a metallic calx which dissolves in the acid. If the acid is concentrated (nitric acid or sulphuric acid) the phlogiston unites with the acid and a phlogisticated nitric or sulphuric acid is produced (nitrous or sulphurous acid). The explanation of the reduction of the calces by means of hydrogen was very simple: what occurred was merely the taking up of and the combination with phlogiston, whereby the metal was regenerated.

These ideas, in which we must recognise a touch of genius, were pretty generally adopted by the phlogistians of the period. They furnished the last glimpse of sunshine accorded to the theory. The same person who discovered the facts which rendered their advancement possible, soon afterwards furnished the experiments which brought about the downfall of the theory.

The phlogiston theory, in the sense understood by Cavendish and Kirwan, was, however, easily disposed of. It explained the conversion of the metals into their calces by means of acids—a matter which had begun to present difficulties to the older phlogiston theory, but it no longer took cognisance of the real phenomena of combustion. In the calcination of a metal, where did the phlogiston (the hydrogen) go to? A previous assertion made by Scheele[15] that during the combustion of sulphur in air, the air takes up phlogiston and unites with it, whereby its volume is diminished, was easily refuted now when the properties of phlogiston (*i.e.*, of hydrogen) were known; and the phlogiston theory thus became, in its new form, no longer applicable to that class of phenomena which it was advanced in the first instance to explain.

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[13] Kopp, Geschichte. 3, 152.

[14] Ibid. 1, 242.

The facts which contributed to the fall of this theory multiplied from year to year. In 1774, Bayen found that mercuric oxide was converted into mercury on heating. Whence came the phlogiston which was required to bring about this change? Bayen perceived the importance of his discovery, and regarded mercuric oxide as different from the metallic calces proper. He found at the same time that the loss of weight in the reduction of the mercuric oxide was equal to the weight of the air obtained. How little attention was, in general, bestowed upon a fact so important, is proved by the views of Macquer who assumed that there must be a loss of weight in connection with the oxidation and the subsequent reduction of a metal. When Lavoisier came forward at a still later date, in opposition to the phlogiston theory, Macquer stated that the news that important facts had been discovered, adverse to the phlogiston theory, caused him some concern, but that he was quite composed again when he ascertained that it was merely a question of relations by weight.[16]

Others, however, thought differently; and Tillet, after having again confirmed the increase of weight during the formation of litharge from metallic lead, drew attention, in a report to the French Academy in 1762, to the circumstance that the explanation of this remarkable fact had not yet been given ; but that it was to be hoped that the immediate future would furnish some elucidation of the matter.[17]

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[15] Kopp, Geschichte. 3, 201.

[16] Dumas, Leçons. 133.

On the discovery of the composition of water the phlogiston theory was, in my opinion, no longer tenable, and had of necessity to be abandoned, since another theory, which was in conformity with all the facts, was ready to hand.

The fact that defenders of Stahl's views were still to be found from ten to fifteen years later proves, however, how difficult it is to eradicate prevailing opinions. It shows us how conservative we are by nature, and should make us use every endeavour to shatter our own faith in authority.

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[17] Kopp, Geschichte. 3, 129-130.

LECTURE II.

REVOLUTION OF THE VIEWS REGARDING COMBUSTION—PRIESTLEY—SCHEELE—LAVOISIER—INDESTRUCTIBILITY OF MATTER.

A STRUGGLE of great importance for chemistry was carried on between the years 1774 and 1794. This struggle was concerned with the removal of the fetters laid by the Greek philosophers upon the thinkers of that period, and with the consistent upholding of the Baconian philosophy. It had to do with the recognition of the experimental method (or the method of observation under definite conditions) as the basis of all theoretical conclusions and speculations, and with the clearing away of those prejudices which had been created in the minds of the period by the method followed for centuries—that, namely, of giving the foremost place to speculation, and of adapting observed facts, as well as might be, to the established system.

These twenty years are not only rendered conspicuous by a series of brilliant experimental investigations, but they possess also a universal importance in chemistry because they led to the establishment and recognition of a principle which constitutes the basis of all our chemical experiments ; and which is to so great an extent involved in our general scientific considerations, that deviations from it seem inconceivable to us. This is the principle of the Indestructibility of Matter. It is only with the greatest effort, and from an extremely objective standpoint, that we are in a position to understand scientific treatises in which this basis is wanting.

Although innumerable experiments are in agreement with this principle, yet we must be doubly careful in the adoption of any such law, seeing that it constitutes the basis of all our scientific views. Even here, we must not commit ourselves to any blind belief, neither must we regard this law as absolutely exact; and, however difficult we may find it to build up a scientific edifice without it, still we must never forget that, just like all other laws, it is merely the expression of facts which we have observed; that there are errors connected with all our observations; and that on this account the possibility is not excluded that succeeding centuries may reject the law itself.

Meanwhile, however, we must regard this law as the greatest achievement of chemistry, and as one of the firmest supports of all natural science; while from the period of its general acceptation we date the commencement of a new era in chemistry; that is, of the chemistry of to-day. It will thus be understood why I desire to direct most especial attention to the period at which this law was stated and was put to the test; and why I enter upon a detailed account of Lavoisier's experiments, from which the accuracy of the principle was deduced.

Many hold the view that the reorganising effect which our science experienced, is to be attributed to the discovery of oxygen, which fell—not altogether fortuitously—within the period mentioned. This is not the case, however; and the history of chemistry itself furnishes proof of the fact, inasmuch as Priestley and Scheele were the discoverers of oxygen, while Lavoisier was the reformer of chemistry. I cannot resist the temptation to point out how the endeavour was made to bolster up phlogiston, and how Priestley and Scheele made every conceivable effort to bring the astonishing properties of oxygen into harmony with the existence of phlogiston (which had never yet been demonstrated).

Priestley discovered oxygen in 1771. He isolated and examined it, and the priority of the discovery is his. He published a detailed account of it in 1775.[1] Scheele's investigation appeared two years later, but it has been shown that his experiments were independent of and nearly simultaneous with those of Priestley.[2] Both chemists employed almost similar methods for its preparation. They obtained it from mercuric oxide, pyrolusite, minium, nitre, etc. Lavoisier also wrote a treatise on oxygen, but Priestley states that he had previously informed Lavoisier of his discovery, although the latter makes no mention of this.[3] It is to be deplored, but unfortunately it seems to be established, that Lavoisier repeatedly tried to appropriate to himself the merits of others. I do not enter further into this matter here, because I regard it as inessential in the history of the development of chemistry. A man's own period is concerned with his personal qualities, and history with his works. Lavoisier paid with his life both for faults which he committed and for faults which he did not commit. His own time judged him. Posterity may regard him with admiration and indulgence.

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[1] Priestley, Experiments and Observations on different kinds of Air, Vol. 2, London (1775), 29; Alembic Club Reprints, No. 7, 5.

The different views which were held with respect to oxygen by its discoverers are of interest to us.

Priestley, the worshipper of chance, who asserts that his greatest discoveries are due to the latter only, and for whom every new experiment is a source of new surprises,[4] describes in detail how he discovered oxygen and studied its properties. He recognises that combustion proceeds better in this gas than in any other, and assumes, further, that atmospheric air owes its property of supporting combustion and respiration, to the presence in it of the gas which he has discovered. He finds, moreover, that it is absorbed by nitric oxide, whence he derives a method of determining the quantities of oxygen in mixed gases. What does he conclude from all this, however; how does he explain these phenomena? According to him, when a substance burns its phlogiston must be able to separate from it.[5] But in order that this may take place the phlogiston must find another substance with which to unite. Combustion is possible in air; therefore air can take up phlogiston, but that only to a certain extent, for after some time it becomes incapable of supporting combustion any longer. It is then saturated with phlogiston. Substances burn in the oxygen gas discovered by Priestley better than they do in air: it is *dephlogisticated air* (a name which Priestley proposes for the new substance) or air deprived of phlogiston, and it is thus better fitted for taking up phlogiston than ordinary air is. The nitrogen, on the other hand, which remains behind after the oxygen of the air has been absorbed (and with regard to which Priestley is aware that it supports neither combustion nor respiration) is air saturated with phlogiston, or, *phlogisticated air*. With Priestley the existence of oxygen was no argument against the assumption of phlogiston, which he defended till the end of his life. Thus we find him early in the nineteenth century, when the majority of chemists had given up the phlogiston theory, addressing letters to the French Academy from America (whither he had withdrawn, chiefly on account of his political opinions), in which he requests refutation of his views.[6] This was not difficult to give, and although it was refused him by the learned French Society, I must not omit to point out what is fallacious in his mode of regarding the matter.

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[2] Nordenskjöld (see Carl Wilhelm Scheele, Nachgelassene Briefe und Aufzeichnungen, Stockholm (1892), xxi.) even endeavours to prove that the priority belongs to Scheele rather than to Priestley, but with this I do not agree. [3] Priestley, The Doctrine of Phlogiston established and that of the Composition of Water refuted. Northumberland (1800), 88. [4] Priestley, Experiments, etc., **2**, 29, 39, 42, etc.; A.C.R. **7**, 5, 12, 15, etc.

"When a substance burns in air, the latter becomes phlogisticated"—if we burn phosphorus, we obtain phosphoric acid (or phosphorous acid), while nitrogen, the phlogisticated air, remains behind. But if we burn a candle or coal, we obtain a mixture (consisting of nitrogen and carbonic anhydride), part of which can be absorbed by means of alkali, thus exhibiting a phlogisticated air, possessed of properties different from those of the preceding one. If we burn phosphorus in dephlogisticated air, nothing at all remains behind—the phlogisticated air vanishes. The contradictions to which Priestley's system leads, become manifest when it is applied to the facts known even at that period. Priestley failed to recognise this, because his general chemical knowledge was small;[7] because he placed no value upon the results obtained by others; and because he uniformly defended, with the most dogged persistence, the ideas which he once adopted.

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[5] Kopp, Geschichte. I, 242. [6] Dumas, Leçons. 115. Priestley, The Doctrine, etc. x. and xii.

What, on the other hand, were Scheele's theoretical views; how did he regard oxygen? Scheele—the ideal of a pure experimental chemist, the discoverer of numberless substances, a man who carried out the most difficult investigations with the most slender resources, who possessed in the highest degree the faculty of observation, so that an error can scarcely be found in any of his very numerous researches; Scheele, who does not, as happens to-day even with the best and most capable observers, overlook half of the points, but grasps the phenomena in their entirety and examines them one by one, and for whom every new experiment forms a mine of great discoveries—what intellectual progress did he introduce into our science?

I must, unfortunately, reply that this was very small. His general views are so confused that I only enter with reluctance upon the task of giving an outline of them.

Scheele laid down his views chiefly in a small work on "Air and Fire." The principal difficulty in giving an account of his opinions is due to the fact that phlogiston, the basis of them, is an unknown substance, to which he can assign every possible property; so that sometimes he endeavours to identify it with an element which is known to us, while at others he seeks to place it side by side with the medium which the physicists call ether. In consequence, it often seems as if Scheele adopted the hypothesis of Cavendish and Kirwan, and by phlogiston understood hydrogen,[8] and yet, on the other hand, this is not in accord with many of his other views. With him phlogiston is, generally speaking, a subtle substance weighing but little, and concerning which he assumes that it is capable of penetrating the walls of his vessels. He regards oxygen as a compound of water with a hypothetical saline substance,[9] in which compound there is, according to him, very little phlogiston. During combustion, the phlogiston of the combustible substance escapes, along with this saline substance from the oxygen, in the form of heat and light; the other constituent of the combustible substance—the metallic calx, for instance—remains behind, united to the water of the oxygen. With Scheele, hydrogen is almost pure phlogiston, which, however, contains a small quantity of that hypothetical substance (matter of heat) which is also present in oxygen. When hydrogen is burned with oxygen, the water of the latter separates, and the matter of heat from the oxygen unites with the hydrogen—the compound of phlogiston with little of the matter of heat—and produces heat and light. Thus it was only necessary to add some of that hypothetical substance to hydrogen in order to convert it into heat or light.

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[7] Kopp, Geschichte. I, 239. [8] Ibid. I, 262. [9] Ibid. I, 261.

Scheele's views are at variance with all the relations by weight, about which he troubled himself very little. In accordance with his views, the metallic calx, for instance, should weigh less than the metal plus the oxygen consumed; since the phlogiston of the former escapes, in combination with the matter of heat from the latter, as heat and light. The assumption of a ponderable matter of heat, which plays a great part in his arguments, was at variance with the earlier experiments of Boerhaave (compare p. 8), so that Scheele, in his theoretical views, came nearer to those who would retain Stahl's doctrine at any cost, than to those who desired an explanation of the observed facts, free from preconceived ideas. I leave these, however, and I do so all the more willingly, because I now wish to turn to the ideas and observations of Lavoisier, which are accessible and comprehensible to every one, and constitute the basis of the chemistry of to-day.

It is not requisite that I should enumerate and describe all the researches of this accomplished investigator; this would exceed the claims which any one could make, in such a historical sketch as I intend to give. On the other hand, the importance of the philosopher with whom I have now to deal, requires that he should be treated of apart from his contemporaries.

The characteristic which distinguishes his researches from those of most of the other chemists of his time, is the systematic consideration of the quantitative relations, which constitutes, in his hands, a decisive criterion with respect to phenomena. Before Lavoisier's time—and I recall this intentionally—Rey,[10] and after him, Hooke[11] and Mayow,[12] had turned their attention to the increase in weight on combustion. The views which they stated, come very close to the correct explanation of the process—Mayow approaching nearest to the truth. In Mayow's opinion the real substance which affects combustion is the "nitro-aerial spirit" which is present in the air and unites with the metal during calcination. (The name of this substance is intended to recall its occurrence both in nitre and in the air.) For any process of combustion there are requisite, according to him, not only inflammable particles (which he designates "sulphureous particles"), but also the presence of this nitro-aerial spirit, the taking up of which explains the increase in weight.[13] The establishment of the phlogiston theory, which occurred at this period, and the acceptance that it met with, show to how small an extent these views were then understood, or, indeed, definitely established.

Notwithstanding this, the priority in the mode of explaining the process of combustion cannot be claimed for Lavoisier. At the same time, the latter did not obtain his views from the chemists above mentioned, whose works were not widely disseminated, and were disregarded. But what places Lavoisier before any of them is the fact that he not only stated, as they had done, an idea which could be employed to explain some phenomena, but that, with the balance in his hand, he also vindicated, by means of a series of brilliant investigations, the universality of the principle of the conservation of matter. He thus proved that he possessed not only a speculative head, but that he was also a scientific thinker and worker, who tested his views by means of intelligently conceived experiments, and, from these, further created new ideas.

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[10] Alembic Club Reprints, No. 11. [11] Ibid. No. 5. [12] Ibid. No. 17.
[13] Kopp, Geschichte, 3, 135.

It cannot be asserted, at least I have not been able to read it out of his works, that Lavoisier stated the principle of the indestructibility of matter as an axiom. But he recognised the truth of the law; for why, otherwise, should he have had constructed for one of his first investigations, "On the Conversion of Water into Earth," a balance which surpassed in accuracy everything that was known at the time in such instruments? He recognises the truth of the principle, but he does not state it. Proof is to be sought in experiments, and not in words, and so he holds back until a suitable opportunity; just as he held back the attack upon the phlogiston theory until he saw that the moment had arrived when, with a single blow, he could overthrow the house of cards, held together as it was by decaying preconceived notions only. Accordingly we find his ideas about this fundamental doctrine expressed in his works only here and there, where it is necessary for him to furnish, at once, grounds for an opinion, the experiments in support of which are not yet completed. An instance is furnished, for example, in his first treatise on the composition of water (which substance he finds to consist of hydrogen and oxygen), where he would like to prove that the weight of the water produced by the union of hydrogen and oxygen is equal to the sum of the weights of the two gases employed—a point which he had not, at that time, established by experiment. He there states that this necessarily follows, since the whole is equal to its parts,[14] and nothing but water is produced by the combustion. At that time the priority of this discovery was disputed, and had, without injustice, been ascribed to Cavendish and not to Lavoisier. As it appears from a letter of Blagden's[15] and also from a letter from Laplace to De Luc,[16] Lavoisier was acquainted with Cavendish's investigation prior to his own experiments, and hastened to publish his results. It is in this way that we obtain knowledge of a fundamental doctrine which had long been clear to him, but which was only at once adopted by a very few chemists. At a later date Lavoisier expresses himself still more distinctly, stating that the substances employed and the products obtained can be brought into an algebraical equation ; and that if any term is unknown it can be calculated.[17] This is the first idea of those equations which we now employ daily.

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[14] Lavoisier, Oeuvres. **2**, 339.

[15] Crell's Annalen. 1786, **1**, 58.

[16] Kopp, Beiträge. **3**, 271.

Still we do not foresee the course of the development of this great thinker's ideas, if we follow him, in a general way at least, from his first experiments onwards. It may be said, however, that the development of his views is that of the chemistry of his period.

One of Lavoisier's earliest investigations deals with the supposed conversion of water into earth.[18] He points out the inaccuracy of this supposition, which was generally held at the time. It is interesting to follow him in his experiments. He seals up a quantity of water in a glass vessel, which was known at that time as a pelican and is so arranged that a glass tube which is fused on to its neck above, leads the condensed water back again into the body of the vessel. He weighs this empty, and then with water in it, after closing the single opening by means of a glass stopper. He then distils the water for a hundred days. The formation of earth appears after a month, but he proceeds with the distillation until the quantity formed seems to be sufficient. He now weighs the apparatus again, and finds it to be just as heavy as before ; whence he concludes that no fire material has penetrated it ; for otherwise, he considers that the weight must have been increased. He next opens it, weighs the water along with the earth, and finds its weight increased, but that of the glass diminished. This leads him to the assumption that the glass has been attacked by the water, and that the formation of earth is not a conversion but a decomposition. His conclusions accord exactly with his experiments ; yet he does not permit himself to be blindly led by them. Thus he finds the increase in the weight of the water to be a few grains more than the decrease in the weight of the glass. Another person might perhaps have concluded from this that there had been a production of matter; Lavoisier, however, explains it as an error of experiment. Although this is a bold view for the period, yet it shows that he is guided by profound ideas, and understands how to criticise his own experiments. All later investigations have confirmed the accuracy of his explanation.

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[17] Dumas, Leçons. 157.

[18] Lavoisier, Oeuvres. 2, 1.

Scheele,[19] on his part, was occupied about the same time with similar investigations, and arrived at the same results; but the mode in which the Swedish chemist conducts the experiment is very different. He analyses the earth and finds that it consists of the same substances as the glass in which the water was heated.

A later paper of Lavoisier's treats of the increase in weight on combustion. As early as 1772, he hands in to the French Academy a sealed paper, in which he shows that the products of the combustion of phosphorus and sulphur are heavier than the substances burned. This he attributes to an absorption of air (of air, because oxygen had not then been discovered).[20] In an investigation on the calcination of tin,[21] he causes this operation to take place in closed vessels; these he weighs before and after, without observing any difference; whence he concludes that no fire material is taken up. He shows, further, that the metal has increased in weight by just as much as the air has lost.

Oxygen is discovered shortly afterwards, whereupon Lavoisier repeats the experiments of Priestley and of Scheele; but his conclusions are totally different from those of the two other chemists. He is already prepared for this discovery, and, with him, it becomes the foundation of a new theory. Oxygen he at once recognises as that part of the air which unites with the combustible substance during its combustion; and he calls it "*air éminemment respirable.*" In the same paper he shows that fixed air is a compound of carbon with this air, and that the latter is also contained in nitre.[22]

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[19] Dumas, Leçons. 129. [20] Lavoisier, Oeuvres. 2, 103. [21] Ibid. 2, 105. [22] Ibid. 2, 128.

Some time afterwards, in 1777, he advances a complete theory of combustion.[23] He says:—

1. Heat and light are disengaged during every combustion.

2. Substances burn only in pure air.

3. This is used up in the combustion, and the increase in weight of the substance burned is equal to the loss in weight of the air.

4. The combustible substance, by its combination with pure air, is usually converted into an acid; the metals, on the other hand, are converted into metallic calces.

In a paper on the composition of nitric acid, Lavoisier tries to prove, in the case of this acid also, the last of the above statements, which is of importance later when we come to deal with theories of acids.[24] He there shows that this acid contains oxygen, while he is not aware that it contains nitrogen. The latter fact was discovered a few years afterwards by Cavendish, on passing electric sparks through mixtures of oxygen and nitrogen,[25] whereby nitric acid was obtained.

Lavoisier at this time groups together the facts that carbonic acid (carbonic anhydride) consists of carbon and oxygen, sulphuric acid (sulphuric anhydride) of sulphur and oxygen, phosphoric acid (phosphoric anhydride) of phosphorus and oxygen, and nitric acid of "*air nitreux*" (nitrous air, *i.e.* nitric oxide) and oxygen. He further shows that an acid is obtained by treating sugar with nitric acid (that is, by supplying oxygen), and from this he concludes that Priestley's dephlogisticated air must contain the acidifying principle (*Principe acidifiant—principe oxygine*).[26] From this time onwards, he regards all acids as consisting of a basis, or radical, and of this *principe oxygine*. His "*air pur*," on the other hand, besides this acidifying principle, contains also the "*matière de chaleur*" (matter of heat).

It is certainly remarkable to find even Lavoisier speaking of a fire material, which he afterwards designates "*calorique*," and of which I shall explain the signification.

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[23] Lavoisier, Oeuvres. 2, 226. [24] Ibid. 2, 129. [25] Kopp, Geschichte. 3, 231. [26] Lavoisier, Oeuvres. 2, 249.

The "*matière du feu*" is not possessed of weight. Lavoisier shows this by burning phosphorus in closed vessels, whereby heat is liberated but no loss of weight takes place.[27] Further, he causes water to freeze in closed vessels, and here, likewise, he finds no change of weight. Since he is aware, from his own experiments, that heat is disengaged in the process, he considers that he is justified in assuming that heat has no weight. A better notion of what Lavoisier calls "*matière du feu*" will be obtained by my stating his views on the constitution of matter, which I take from his "Réflexions sur le Phlogistique."[28] According to him, matter consists of small particles which do not touch one another, since, otherwise, a diminution of volume by lowering of temperature could not be explained:[29] the matter of heat exists between these particles. The hotter a substance is the more of the matter of heat does it contain. In the investigations into the specific heats of various substances, carried out along with Laplace, Lavoisier further proved that, for a like increase in temperature, substances do not take up like quantities of the matter of heat.[30] Into the consideration of these experiments, as well as of those on the heat of combustion,[31] I do not enter here. Lavoisier knows that, by the addition of heat, ice is first converted into water, and the water then into steam. Hence gases contain most of the matter of heat. This is what we should understand when he says that his "*air pur*" consists of the acidifying principle and the matter of heat. During combustion the former unites with the combustible substance, and the matter of heat is liberated. It produces heat and light.

The following statement is very characteristic of Lavoisier's standpoint:—[32] "Heat is the energy which results from the imperceptible movements of the molecules of a substance; it is the sum of the products of the mass of each molecule into the square of its velocity." Here we find him in complete agreement with the fundamental doctrines of the mechanical theory of heat. His views with respect to the heat disengaged during combustion, although not quite accurate, are also of great importance. He considers[33] that when a solid substance (phosphorus) burns in a gas (oxygen), and the product of the combustion is solid (phosphoric anhydride), the disengagement of heat is due to the condensation which the gas has undergone, in order that it may become solid. If the product is gaseous (carbonic anhydride), he attributes the disengagement of heat to the alteration of the specific heat. He advances the general view that the heat of combustion must be greatest when two gases unite to form a solid substance. How correctly he understood the application of these fundamental ideas, is shown by his mode of explaining the lowering of temperature produced by dissolving salts in water. Lavoisier assumes, as we do, that it is the change of state of aggregation which occasions the absorption of heat.[34] He shows, further, that the evolution of heat which occurs on mixing sulphuric acid with water, is accompanied by a decrease in volume, and that both maxima coincide ; so that theory and experiment agree.

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[27] Lavoisier, Oeuvres. **2**, 618.
[28] Ibid. **2**, 623.
[29] Compare also Lavoisier, Traité de Chimie. **1**, etc.
[30] Lavoisier, Oeuvres. **2**, 289.
[31] Ibid. **2**, 318 and 724.
[32] Ibid. **2**, 286.

I must not, however, enter too deeply into these matters, which belong, partly at least, to physics ; and, therefore, I return to his purely chemical investigations.

Lavoisier adheres to Boyle's definition of an element,[35] which we retain to-day. With him, an element is any substance which cannot be further decomposed.[36] What the significance of this definition is, and of what importance this idea of an element has become for the whole of natural science, has been specially pointed out by Helmholtz.[37]

The metals were first regarded as elements by Lavoisier.[38] In a long paper he disputes the prevailing view, which assumed the existence of phlogiston in the metals. These interesting disquisitions, which contain the annihilation of the preceding system, only appear towards the end of his short and brilliant scientific career. At first there was no explanation forthcoming for a series of phenomena which were in agreement with Kirwan's phlogiston theory. I refer to the behaviour of the metals towards acids; to the hydrogen liberated; and to the reductions carried out by Priestley by means of hydrogen. It is only after the composition of water has been ascertained by Cavendish, Watt, and Lavoisier,[39] that Laplace arrives at the idea (as Lavoisier relates[40]) that on dissolving metals by means of acids, water is decomposed—that the hydrogen is, therefore, evolved from the water, while the oxygen of the latter unites with the metal to form an oxide. The phenomena of reduction now become clear also. The hydrogen unites with the oxygen of the metallic oxide, forming water, and the metal remains behind. Lavoisier tries to prove all these points by a series of excellent experiments. His investigations upon the decomposition of water, are, especially, of extreme interest.[41] He passes water vapour over weighed iron turnings, heated to redness, and collects the hydrogen in an eudiometer. In this case also, he weighs everything—the water, the gain of the iron, and the hydrogen. In this way, he succeeds in finding out the quantitative composition of water; and the latter, along with the quantitative composition of carbonic anhydride, which he determines somewhat later,[42] constitute the starting point for his researches on organic analysis.[43]

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[33] Lavoisier, Oeuvres. **2**, 647. [34] Ibid. **2**, 654. [35] Kopp, Geschichte. **2**, 275. [36] Méthode de Nomenclature Chimique. Paris (1787), 17. [37] Tageblatt der Naturforscherversammlung in Innsbruck, 1869, 37. [38] Lavoisier, Oeuvres. **2**, 623.

I wish to say at least a few words with regard to these researches; since, even although the numbers obtained are not very exact, the methods are so important that I cannot pass them by unmentioned.

Lavoisier places a weighed piece of charcoal in a dish, under a bell-jar containing a measured volume of oxygen, and standing over mercury. Besides the charcoal, the dish contains a trace of phosphorus and tinder. By means of a bent, red-hot, iron wire, he ignites the phosphorus, which communicates the combustion to the tinder, and thus to the charcoal. After the combustion of the latter has ceased, he takes out the dish and weighs it, and so finds the quantity of the charcoal burned. He measures the volume of gas in the bell-jar, absorbs the carbonic anhydride by means of potash, and measures again. In this way he obtains the volumes of the carbonic anhydride produced and of the oxygen employed in the combustion; and hence, all the data necessary to calculate the composition of carbonic anhydride.

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[39] With respect to the part played by each in this most important discovery, compare Kopp, Die Entdeckung der Zusammensetzung des Wassers. Beiträge. **3**, 235. [40] Lavoisier, Oeuvres, **2**, 342. [41] Ibid. **2**, 360. [42] Ibid. **2** 403. [43] Ibid. **2**, 586.

This he makes use of in carrying out the analysis of organic substances, such as spirit of wine, oil, and wax. He had satisfied himself, at an earlier date, that water and carbonic anhydride are alone produced by the combustion of these substances, whence he had quite correctly concluded that they contain carbon, hydrogen, and oxygen only. In the estimation of their quantitative composition, Lavoisier employs an apparatus similar to that indicated above. For example, he places a spirit lamp, which he weighs before and after, under the bell-jar, and burns some of the spirit; he also determines the quantities of carbonic anhydride produced and of oxygen employed, and from these data he is able to calculate the composition of the spirit.

With this I shall close the consideration of Lavoisier's chemical investigations. A superficial estimate of his merits is all that I have been able to give. It is only by a minute study of his works that any complete idea of his significance, and any proper understanding of how much our science owes to his great intellect, can be obtained. There are, however, certain directions of his activity that I have not even mentioned, as, for example, the researches on respiration, about which I still wish to say a few words. Priestley already knew that oxygen was necessary for respiration.[44] Lavoisier shows how it is used up in the lungs, in the formation of carbonic anhydride and of water, and how this process, which he properly classes as one of combustion, furnishes to man the heat necessary for his existence.[45] He demonstrates that the expired carbonic anhydride derives its carbon from the blood itself; that in the process of respiration we thus, to a certain extent, burn ourselves, and would consume ourselves if we did not replace, by means of our food, that which we have burned. Since he next finds, by special experiments, that in strained activity the breathing is hastened, and that the consumption of carbon is thereby increased, he arrives at the conclusion that the poor man, compelled as he is to work, consumes more carbon than the indolent rich man; but that the latter, by an unfortunate circumstance in the division of worldly possessions, can satisfy his smaller requirements—and that too by means of better food—much more readily than the poor workman can. He therefore calls upon society to remedy this evil by means of its institutions, to improve the lot of the poorer classes, and in this way to smooth away, as far as possible, those inequalities which apparently are established in nature. He closes this ingenious treatise with the words :—[46]

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[44] Compare p. 17.

"It is not indispensable, in order to deserve well of humanity and to pay his tribute to his country, that a man should be called to those public and pompous functions which co-operate in the organisation and regeneration of empires. The physicist, in the quiet of his laboratory and of his study, can also exercise patriotic functions; he can hope to diminish by his labours the many ills which afflict the human species, and to increase human pleasures and prosperity. And if he should only contribute, by the new methods which he may have shown, to the lengthening of the mean age of man by a few years, or even by a few days, he also may aspire to the glorious title of benefactor of humanity."

His own time rewarded him badly for his endeavours.—Four years later, in 1794, he was guillotined by order of the Revolutionary Committee.

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[45] Lavoisier, Oeuvres. **2**, 331.

[46] Ibid. **2**, 703.

LECTURE III.

CHEMICAL NOMENCLATURE — TABLES OF AFFINITY — BERTHOLLET'S VIEWS—CONTROVERSY REGARDING CONSTANT COMPOSITION.

IT will readily be understood why a new era dates from Lavoisier, and why the latter is designated the reformer of chemistry, if we consider what were the theoretical views held before his time, and what they were at the period of his death.

Lavoisier lived to have the satisfaction of seeing his views generally recognised, in France at least; they gradually gained ground also in England and in Germany, where his works were translated, so that it may be justly said that phlogiston, at the beginning of the nineteenth century, had disappeared from scientific works.

Lavoisier not only overthrew the old theory, but it is his chief merit that he introduced a new one in its place, and it is perhaps advisable to state here the most important heads of his theory.

1. In all chemical reactions it is the kind of matter alone that is changed, whilst its quantity remains constant; consequently, the substances employed and the products obtained may be represented by an algebraic equation in which, if there is any unknown term, this may be calculated.

2. In the process of combustion the burning substance unites with oxygen, whereby an acid is usually produced. In the combustion of the metals, metallic calces are produced.

3. All acids contain oxygen, united, as he expresses it, with a basis or radical which, in inorganic substances, is usually an element, but in organic substances is composed of carbon and hydrogen, and frequently contains also nitrogen or phosphorus.

If we contrast these three statements with the views of the phlogistians, *i.e.*, with the theories which prevailed prior to Lavoisier, we shall appreciate the reformation introduced by him into chemical science. The direction of chemical thought was entirely changed, and the facts hitherto ascertained appeared in a new light. It was necessary, in a sense, to translate them in order to understand them, and as it was recognised that a new language was required for their proper comprehension, the need of a system of chemical nomenclature made itself apparent.

I pass over all the attempts which had been made prior to this period to secure a uniform mode of expression, as these did not lead to any results worth mentioning, and as they occurred during a period to which I can only slightly refer. I wish, however, to mention that Bergman repeatedly approached the French chemists with a view to securing uniformity in the naming of substances. In 1782 Guyton de Morveau, probably stimulated by Bergman's suggestions, travelled to Paris, and laid before the Academy there a proposed system of chemical nomenclature. This system contained much that was new and good; but it could not secure the approval of the principal chemists of the period, as it assumed the existence of phlogiston, which even at that time was vigorously disputed by Lavoisier. The latter afterwards succeeded in convincing Guyton of the accuracy of his new views. Guyton agreed to reconstruct his system, and in 1787, in conjunction with Lavoisier, Berthollet, and Fourcroy, he published the *Nomenclature Chimique.* As this system embodies the principles and constitutes the basis of the chemical nomenclature now employed, I cannot pass it by without mention, and I shall therefore state at least its more important features. In doing so, it will frequently be necessary to employ French words. For practically all of these there are exact English equivalents.

Substances are all divided into elements and compounds. Amongst the former there are included all those substances which could not then be further decomposed, and these are classed under five headings. Of these headings the first embraces those bodies which are of very common occurrence, and whose behaviour seems to indicate that they are not decomposable. Examples of these are:—1, Heat (*Calorique*); 2, Light; 3, Oxygen; 4, Hydrogen; 5, Nitrogen (*Azote*). The second class contains the acidifiable bases, such as sulphur, phosphorus, carbon, etc. The third embraces the metals; the fourth the earths; and the fifth the alkalies, which, as is well known, had not at that time been decomposed. The names of the substances belonging to the second, third, and fourth classes are for the most part unchanged; the alkalies are called potash, soda, and ammonia.[1] For all these substances, which, with the exception of ammonia, were regarded as elements, the authors observed the principle of designating each by a single word.

The radicals constitute an appendix to the elements. These are substances which they regard as decomposable, but which exhibit certain resemblances to elementary bodies.

Next come the binary substances, consisting, as they do, of two elements. The acids occur in this class. According to the theory of Lavoisier, the acids all contain oxygen. Their names are in each case composed of two words, of which the first is common to them all and indicates their acid character (*acide*), while the second is a specific name indicating the element or radical occurring in each. Thus we have *acides sulfurique*, *carbonique*, *phosphorique*, *nitrique*, etc. Two acids containing the same element or radical are distinguished by the different termination of the specific name; that containing the smaller proportion of oxygen receiving the termination *eux*, whereby such names as *acides sulfureux*, *nitreux*, etc., are obtained.[2] Hydrochloric acid is called *acide muriatique*, and the existence of oxygen in it is assumed; while oxygen is supposed to be present in still greater quantity in chlorine—the *acide muriatique oxigené*.[3]

The names of the binary substances of the second group, *i.e.*, of the basic compounds containing oxygen, are formed in a manner exactly similar. For these the general designation *oxides* is introduced, and to this word the specific name is appended in the genitive; for example, *oxide de zinc*, *oxide de plomb*, etc.

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[1] Nomenclature Chimique. 67.

[2] Ibid. 85-86.

[3] Ibid. 87.

The remaining binary compounds are distinguished as sulphur, phosphorus, carbon, etc., compounds, and receive the class names: *sulfures*, *phosphures*, *carbures*, etc.

Compounds of the metals with one another are called *alliages* (alloys), the expression *amalgames* being retained, however, for mercury alloys.

Amongst the ternary compounds, the salts alone need be mentioned. They obtain their class names from the acids from which they are derived, and are called accordingly: *sulfates*, *nitrates*, *phosphates*. The termination *ate* becomes *ite* when the salts are derived from the acid poorer in oxygen instead of from that richer in oxygen. The name of the base is appended; for example, *sulfate de zinc*, *de baryte*, etc. When the salt has an acid reaction, the word *acidule* is employed; on the other hand they call basic salts *sursaturé de soude*, etc.[4] Relatively few double salts were known at that time. The designation introduced for these was not very convenient; for example, tartar emetic was called "*tartrite de potasse tenant d'antimoine*"[5] (tartrate of potash containing antimony).

This general review may suffice. Berzelius, as is well known, considerably extended these beginnings of a rational nomenclature, and I shall refer to some of his improvements and expansions when considering his period.

On comparing the science of to-day with what I stated in the preceding lecture regarding Lavoisier's views, it will be possible to judge of the extent to which the latter have been retained. Lavoisier's theories required modification on several points; but on others his ideas were attacked without result, since it has been necessary to return to them again. Thus Lavoisier's theory of acids is now abandoned by the majority of chemists. The introduction of the new views only took place, however, long after his death, and therefore I postpone the consideration of this matter to a later lecture. We must occupy ourselves here with another attack upon Lavoisier, which was eventually decided in his favour, and is of importance on this account, that through it a strict separation of mixtures from compounds was first brought about.

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[4] Nomenclature Chimique. 93 and 97.

[5] Ibid. 52; on p. 235 it is called "tartrite de potasse antimonié" (antimoniated tartrate of potash).

This attack had to do with the question whether chemical combinations are possible in all proportions, or whether substances can combine in certain fixed proportions only. The latter view, as is evidenced by many of his investigations, was assumed by Lavoisier ; and indeed it seems to have been accepted as self-evident by all the chemists of his time, without having been proved. But a book appeared in 1803 which attracted the greatest attention in the scientific world, both on account of its contents and of the form in which these were set forth ; and in this book, amongst other things, the constancy of chemical proportions was denied, on the ground both of theoretical speculations and of experimental investigations.

The work to which I refer is Berthollet's *Statique Chimique*, and if I am to render intelligible the importance of the attack which it contains, I must give at least a slight sketch of Berthollet's extremely interesting general theoretical ideas. I extract these from the work just mentioned, and from some scattered essays by its author upon the same subject.[6]

Berthollet's book will always be of importance in chemistry, chiefly because the fundamental doctrines to which the author subordinates all chemical reactions, are the principles of mechanics and of physics ; and these must necessarily possess a value in chemistry. And even although many of Berthollet's conclusions do not harmonise with experiment, and have long since been disproved, still this does not damage the basis of his conceptions.

The work as a whole is chiefly directed against the false view which had been adopted with regard to the affinities of substances ; and against the misuse which was made at the time of so-called tables of affinity. The latter were tables which purported to express the strength of the affinity of substances, and they had been drawn up by a large number of chemists. The earliest originated with Geoffroy,[7] and dated from the year 1718. It consisted of various tables in which the other substances were so arranged with respect to a particular one, that each preceding substance always decomposed the compound which the next succeeding one formed with this particular substance. Thus, for example, his table for acids in general ran: fixed alkali; volatile alkali; earths; metals. The construction of such tables was one of the chief occupations of chemists in the middle of the eighteenth century. With them they associated the erroneous view that the affinity of one substance towards another is invariable; and it was only by degrees that chemists were convinced that this was an error. In 1773 Beaumé pointed out that the affinities were different at ordinary and at very high temperatures (in the wet and dry ways), and that for each substance it would thus be necessary to construct two tables which should express its behaviour towards all other substances under these two different sets of conditions.[8] Bergman undertook this task,[9] and it is truly astonishing what enormous pains he took in carrying it out. For each substance he constructed two tables, in which he compared its behaviour towards fifty-eight others, and these latter were so arranged that each preceding substance decomposed the compound which the next succeeding one formed with the particular substance concerned. From these tables it was, seemingly, possible to foretell the results of all reactions; hence they were held in great esteem. When a new substance was discovered, such a table of affinity was at once constructed for it, and even Lavoisier respected this usage on the occasion of his investigation of oxygen, although he pointed out at the time that a similar table would really be required for every degree of temperature.[10]

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[6] Ann. Chim. **36**, 302 ; **37**, 151 and 221 ; **38**, 113 ; **39**, 3.

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[7] Kopp, Geschichte. **2**, 296. [8] Ibid. **2**, 299. [9] Ibid. **2**, 301.

[10] Lavoisier, Oeuvres. **2**, 546.

Berthollet, however, is the first to point out the error to which chemists had committed themselves in drawing up these tables. He destroys their significance by advancing the doctrine that the effective action of a substance is related to its mass.

Berthollet illustrates, especially by reference to salts, the laws in accordance with which chemical compounds are formed. He assumes that the same chemical effect is always connected with the neutralisation of any given quantity of a particular base (or acid). He represents this effect as the product of the affinity A, and the saturating capacity S (that is, for example, the quantity of acid necessary to neutralise a unit of weight of alkali). This gives—

$$AS = \text{Constant}$$

$$A = \frac{\text{Constant}}{S}$$

that is, the affinities of two acids are inversely proportional to their saturating capacities,[11] or just the reverse of what Bergman had regarded as correct.[12]

But, according to Berthollet, the quantity Q of any substance present exercises, quite generally, an influence upon the chemical action, which he considers to be proportional to the product of Q into the affinity of the substance. He calls this product the chemical mass.[13] In the case of acids, the chemical mass may also be stated as proportional to the product of the saturating capacity S into Q, the quantity present, as Berthollet likewise points out.[14]

The effects produced by affinity do not, however, depend exclusively upon the chemical mass: they are varied besides by the state of condensation of the substance concerned, and are subject, therefore, to the physical conditions of the experiment (to the pressure, temperature, etc.). As regards the state of condensation of matter, it is, according to Berthollet, a consequence of the two opposed forces, cohesion and elasticity. The predominance of the former brings about the solid state, and that of the latter, the gaseous state ; while in liquids a balance exists between the two. If all acids were in the same state of condensation, then that one should be regarded as the strongest, of which the smallest quantity is necessary to saturate a given weight of a base ; or, as we should now say, of which the equivalent is smallest.

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[11] Berthollet, Statique Chimique. 1, 71; E. 1, 45.

[12] Kopp, Geschichte. 2, 314.

[13] Stat. Chim. 1, 72; E. 1, 45.

[14] Ibid. 1, 16; E. 1, xxiv.

Berthollet applies these principles especially to simple and to double decompositions. According to him, when we add an acid to a dissolved salt, a partition of the base takes place between the two acids in the ratio of their affinities, that is, in the ratio of their *masse chimique*.[15] Both salts and both acids are thus present in the solution ; yet this only holds when both salts possess approximately the same solubility, because a balance is then established which is dependent not only upon the strengths of the acids, but also, and in particular, upon the quantities of each present. He further draws attention to the fact that conviction as to the accuracy of this view cannot be obtained by evaporating the solution and permitting the salts to crystallise out, because as soon as the quantity of water is no longer sufficient for complete solution, the phenomena which take place depend chiefly upon the forces of cohesion and crystallisation, that is, upon the different solubilities of the substances.[16]

Thus, upon crystallising out after mixing a solution of potassium nitrate with sulphuric acid, the more sparingly soluble salt potassium sulphate is alone obtained ; whereas, according to Berthollet, potassium nitrate and potassium sulphate are both present in the solution.

When one salt is much more soluble than the other, it is the less soluble one that is principally formed ; and if one is quite insoluble, there is no partition, but complete decomposition. In this way Berthollet explains, for example, the complete precipitation of barium nitrate by means of sulphuric acid. The barium sulphate, in consequence of its insolubility, is removed from the reaction ; a constantly progressing partition taking place until the whole of the barium sulphate is precipitated.[17]

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[15] Stat. Chim. I, 75 ; E. I, 49.

[16] Ibid. I, 82 ; E. I, 54.

A similar thing occurs in the cases of volatile acids or bases. In this case also a partition takes place, in the ratio of the *masse chimique ;* but as one product (carbonic anhydride, for example) escapes, the decomposition proceeds to the end.[18]

Nevertheless, it is only in cases of extreme preponderance of cohesion (insolubility) or of elasticity (volatility) that complete decompositions are observed. Cases of partial decomposition are far more frequent. Thus, according to Berthollet, calcium salts cannot be completely precipitated by means of oxalic acid.[19]

His views regarding double decomposition are similar. Four salts are, in general, produced in these cases, and the formation of two only is confined to cases where the cohesion, or solubility, is totally different.

This furnishes the explanation of the so-called reversible reactions. Amongst these reactions there are, in the first place, the various crystallisations which may be obtained at different temperatures from the same mixture of salts, if these salts possess solubilities which vary greatly from one another with changes in temperature. Berthollet adduces several examples of this kind,[20] and I shall mention one of them. If a solution contains soda, magnesia, sulphuric acid, and hydrochloric acid, Glauber's salt crystallises out from it at a very low temperature (0° C.), whereas sodium chloride is obtained on evaporation. Hence, at 0°, magnesium sulphate and sodium chloride must change into sodium sulphate and magnesium chloride, whilst at high temperatures the reverse takes place.

In the same way Berthollet is also able to explain the phenomena which are dominated, according to Bergman's views, by the affinities "in the wet and dry ways." Thus, for example, dissolved silicates are decomposed by almost all acids, whereas, on the other hand, silicic acid drives most acids out of their salts at a red heat.

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[17] Stat. Chim. **1**, 78 ; **E. 1**, 51. [18] Ann. Chim. **36**, 314. [19] Stat. Chim. **1**, 78-79 ; **E. 1**, 51-52. [20] Ibid. **1**, 101-102 and 129-130 ; **E. 1**, 71-72 and 395-396.

But Berthollet goes still further. Cohesion determines not merely the nature of the compound formed, but also the proportions in which combination takes place. His conception of a chemical compound is not associated with the constancy of proportions which had been assumed prior to his time. On the contrary, there exist, in his view, chemical compounds with all possible proportions[21]; and it is only special reasons, such, for example, as considerable condensation on combination (that is, change in the cohesion of the constituents), which occasion constant proportions. Thus hydrogen only combines with oxygen in a definite proportion because water, the product of the combustion, is liquid, and the contraction which takes place presents too great an obstacle to the production of other compounds.[22] But if, on combination, there is no change in cohesion, or only a slight change, then compounds are formed with variable proportions. As examples of these he mentions alloys, glasses, and solutions. He says that in these cases the limits are determined solely by the quantities required for mutual saturation, but that, between these limits, the most varying proportions occur.[23]

It will be observed that Berthollet thus classes solutions and alloys amongst compounds, and it will now be understood how he was able to distinguish amongst them some with varying proportions. But it is much more remarkable that Berthollet also assumes variable proportions amongst the oxides. In one of his essays upon the laws of affinity,[24] in which he speaks of metallic precipitations, he assumes, in accordance with his principles, that the two metals distribute themselves over the oxygen: there are thus formed, according to him, oxides containing different quantities of oxygen. He afterwards develops his views upon this point still more clearly.[25] He says: "I have to show, then, that the proportions of oxygen in the oxides depend upon the same conditions as those in other compounds; that these proportions may vary progressively from the limit at which combination becomes possible up to that at which it attains the highest degree." The limits themselves he regards as determined by circumstances of cohesion.—In the same way he believes in the existence of salts with varying quantities of base. If the base is precipitated, by means of an alkali, from a salt with an insoluble base, he supposes that a certain quantity of acid is precipitated along with the base, and that this quantity is variable.[26] In short, compounds with constant proportions are, according to Berthollet, exceptions, and the proportions in which substances combine are, as a rule, dependent upon the conditions of the experiment.

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[21] Stat. Chim. **1**, 373; **E. 1**, 282. [22] Ibid. **1**, 367; **E. 1**, 276. [23] Ibid. **1**. 373-374; **E. 1**, 282-283. [24] Ann. Chim. **37**, 221.

If we summarise Berthollet's views once more, we may say that affinity appeared to him to be a force identical with gravity,[27] whose phenomena are more varied only because it sets the molecules themselves into motion, and its effects are dependent upon the size and shape of the particles. In applying these physical principles to chemical reactions, he arrives at the conception of chemical mass, which he defines as the product of affinity and quantity present. The chemical effects depend upon the magnitude of this chemical mass, and upon the cohesion of the substance, that is, upon its solubility and its greater or less volatility. This then leads him further to two general conclusions:—

1. Tables of affinity are useless, since in them affinity is assumed to be constant and independent of physical conditions.

2. There are compounds with varying and progressively increasing proportions of their constituents.

The first of these conclusions is adopted generally, and we find that the tables of affinity disappear soon after the appearance of Berthollet's *Statique Chimique*. The second, on the other hand, meets with vigorous contradiction; Proust, a fellow-countryman of Berthollet's, especially opposing the views there stated. Thus there arises that renowned controversy between these savants which is remarkable not only for the talent which the opponents exhibit, but also for the extreme politeness which is observed on both sides.

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[25] Stat. Chim. 2, 370; E. 2, 316. [26] Ibid. 1, 86; E. 1, 58. [27] Ibid. 1, 1; E. 1, vii.

Berthollet was at that time held in high esteem by the scientific world. The sagacity which he had manifested in a high degree in the working out of his book was justly admired. It will be understood, then, that it was no small undertaking to attack views which he had stated with much confidence, and had endeavoured to prove by experiments. At the same time I may state here that the experimental part, especially, of the *Statique Chimique* leaves much to be desired. When Berthollet asserts that in the oxidation of the metals oxygen compounds are formed with widely varying proportions, the reason of this is that he analysed the crude product directly, and did not first try to satisfy himself that he was not dealing (as was generally the case) with a mixture. If, in addition to this, the backward condition in which quantitative analysis stood at that time is taken into consideration, it will then be understood how Berthollet arrived at these erroneous results.

Proust, on the contrary, proceeded very cautiously. He endeavoured to find proofs of the purity of his substances, and bestowed the greatest care upon the determination of the constituents. He thus succeeded in discovering the hydroxides, which had hitherto been entirely overlooked[28] and were regarded as oxides containing a special proportion of oxygen. We are indebted to Proust for investigations of the most of the metals, which he usually published under the title *Faits pour servir à l'histoire*, etc.[29] Further, he wrote detailed treatises upon the sulphur and oxygen compounds,[30] in which he shows that many metals form only a single oxide; that many, however, form two; and that in those cases where three oxides exist, the intermediate one can be regarded as a compound of the other two.[31] In the same way, he endeavours to detect the error in Berthollet's view regarding the existence of sulphur compounds with variable proportions of sulphur. In all these investigations he emphasises the distinction between mixtures and compounds. He says that the latter are characterised by quite definite proportions, which hold for compounds occurring in nature as well as for those obtained in the laboratory, and that this *pondus naturæ* lies just as little within the discretion of the chemist as does the law of affinity, which governs all combinations.[32]

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[28] Ann. Chim. **32**, 41; Journ. de Phys. **59**, 347.

[29] Journ. de Phys. **51**, 173; **52**, 409; **55**, 325, 457; Ann. Chim. **32**, 26; **38**, 146; **60**, 260, etc.

[30] Journ. de Phys. **59**, 321; Sulphur compounds, ibid. **53**, 89; **54**, 89; **59**, 265.

But Berthollet also responds by means of facts. He examines the carbonates of the alkali metals,[33] and finds that when the base is saturated by carbonic anhydride under pressure, crystals are obtained which differ in composition from the carbonates previously known. He shows that these give up carbonic anhydride on dissolving and heating, and yield salts differing again in composition. He disputes the fact asserted by Proust,[34] that by leading a trace of carbonic anhydride into an alkaline solution only a few molecules are saturated, while the others remain uncombined. According to Berthollet, a solution of this kind evolves carbonic anhydride on the addition of a drop of hydrochloric acid, and consequently contains a *souscarbonate*,[35] that is, he considers that the trace of carbonic anhydride present is distributed over the whole quantity of the base.

Rendered cautious by Proust's rejoinders and excellent researches, Berthollet now no longer assumes all possible proportions between oxygen and the metals as actually occurring. He limits these to a few; yet, in his examination of the oxides of lead, he asserts that he has isolated four different stages of oxidation which are attained by heating the metal in air.[36] All the same he has thereby moved a step nearer to Proust.

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[31] Journ. de Phys. **59**, 260. [32] Ann. Chim. **32**, 31. [33] Journ. de Phys. **64**, 168. [34] Ibid. **59**, 329. [35] Ibid. **64**, 181. [36] Ibid. **61**, 352.

Still the struggle is not on this account at an end. Even yet Berthollet will not recognise the difference between mixtures and compounds which had been advanced by Proust. For both of these conceptions he demands sharp definitions.[37]

Now, as a matter of fact, Proust cannot furnish these definitions; still he shows how mixtures can be distinguished from compounds in special cases, and in doing so, he succeeds in disproving a great many of Berthollet's statements. Obviously I cannot follow this matter in all its details, and I shall, therefore, only show by a single example Proust's mode of adducing his proofs. Berthollet had previously asserted that, by treating mercury with nitric acid, a series of oxides was obtained, in which the proportion of oxygen increased steadily from a definite minimum.[38] Further, he had observed that these oxides, on treatment with hydrochloric acid, were converted into two chlorides, and had assumed that it was the insolubility of mercurous chloride which caused the oxides to betake themselves from the stage of oxidation at which they stood to the two end stations.[39] Proust considers that too much intelligence is, on this assumption, attributed to the oxides. He shows that in the dry way also, only two chlorides are formed, and that these correspond to the only two oxygen compounds of mercury into which Berthollet's mixtures can be separated.

Thus this controversy, which began in 1801, continues until 1807, but, about this time, the interest that the scientific world had at first taken in the two opponents diminishes considerably. The authority of Berthollet had made it possible that, in consequence of his attack, a doctrine which had previously been regarded as accurate *a priori*, should appear doubtful to many. But the researches of Proust on the one hand, and those of Klaproth and Vauquelin on the other, had restored confidence in that doctrine. Berthollet's rejoinders began to lose their effects. He was forced to admit the existence, in ever widening classes of substances, of compounds with constant proportions; which, as a matter of fact, he had never wholly denied. In 1809 he still regards compounds with variable proportions as possible,[40] but in this opinion he stands isolated. Too much support has now come to the opposing side. Richter's investigations, carried out from 1791 to 1800, had at length become known; Dalton had formulated his atomic theory, which was irreconcilable with Berthollet's view and was already beginning to constitute the basis of chemical considerations; Gay-Lussac's classical work on the proportions by volume in which gases combine was concluded; and Berzelius had published his first important papers. Thus the controversy ends, apparently with the complete defeat of Berthollet.

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[37] Journ. de Phys. **60**, 347. [38] Ann. Chim. **38**, 119. [39] Proust, Journ. de Phys. **59**, 335.

I have treated this subject at length, because I consider it very important. We have here to do with a general doctrine which constitutes one of the foundations of our theoretical considerations, and settles the distinction between mixtures and compounds. It is for the latter alone that our chemical laws hold, since mixtures are not subject to them. In any particular case, therefore, it is very important to know which class of substances is being dealt with. What, then, are our means of forming an opinion?

It is to be found stated in text-books, that compounds possess a homogeneous character, whereas mixtures can very frequently be mechanically separated into their ingredients. It is further stated there that in compounds the properties of the constituents have disappeared, whilst they are present side by side in mixtures. Finally the constancy of proportions is then adduced as characteristic, and I wish to direct attention to this whole matter. There are cases in which mixtures are, in their whole behaviour, no longer distinguishable from compounds. We then have recourse to analysis to solve the question. We prepare the substance in various ways, and observe whether it always possesses the same composition. We thus invert the doctrine discussed by Berthollet and Proust. The former regarded compounds with variable proportions as possible, whilst the latter assumed that substances combine in a few definite proportions only. We call a substance a compound when it contains its constituents in invariable proportions.

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[40] Mém. d'Arcueil. 2 470.

I do not know whether the difference between the two conceptions has been made clear. In order to appreciate the full bearing of the question, a person must himself have required to decide as to whether he had a mixture or a compound in his hands. Even yet we are without a definition which shall suffice for every case; that is, without such a definition as Berthollet repeatedly demanded from Proust. It is true that we have certain means of judging with respect to chemical compounds, as, for instance, capacity for crystallising, and invariable melting point in the case of solids, and constant boiling point in the case of liquids. Yet these are frequently insufficient. I need only recall the phenomena of isomorphism, when we must admit that mixtures also can crystallise. I mention the solutions of hydrochloric acid, hydriodic acid, etc., in water, regarding which Roscoe has proved that they are only mixtures (solutions), and we must admit that these likewise can possess a constant boiling point. In short, this distinction forms one of the most difficult and most important problems, and in point of fact it is often insufficiently attended to. In the study of chemical papers opportunity is often afforded of observing how errors have arisen through neglect of this very matter. How often have formulæ been advanced for substances and theoretical conclusions based upon their existence, before their compound character has been conclusively settled! The purpose of the foregoing remarks is to serve as a warning against any such error, and I therefore hope to be excused for having, for a short time, quitted my proper theme.

LECTURE IV.

RICHTER'S INVESTIGATIONS — DALTON'S ATOMIC THEORY — GAY-LUSSAC'S LAW OF VOLUMES — AVOGADRO'S HYPOTHESIS — WOLLASTON'S EQUIVALENTS.

I SHALL now proceed to describe the development of the atomic theory, up to the second decade of the nineteenth century, in so far as it possesses scientific interest. It is beyond my intention, in doing so, to enter into the hypotheses of the Greek and Roman philosophers regarding the constitution of matter. That Leucippus and Democritus regarded matter as composed of ultimate particles, and that Lucretius afterwards expounded these views at length, merely shows to us, what we have long known, that there were men amongst the Greeks and Romans who might in every respect be placed beside our thinkers of to-day. These philosophers made use of the deductive method of reasoning; they started from general principles, although their conclusions from them were not always in accord with observations. The latter were of relatively small importance, especially as at that time experimentation, or the art of investigation under stated conditions, was practically unknown. For this reason, Democritus cannot be placed in front of Kant, who, starting from the opposite view—from the dynamic hypothesis—constructed the universe in perhaps just as logical a fashion. The expenditure of talent and sagacity which we observe on the part of the supporters of the two views, was in vain; the observations by means of which such questions could be solved, were entirely wanting.

The scientific development of the atomic theory depended simply upon the discovery of a series of facts which were connected together by it, and found in it a simple explanation. It is my business now to mention these experiments, and to give an account of the chemical researches which rendered the assumption of the atomic theory necessary, and which were brought to a conclusion by means of the theory.

In the preceding lecture I dealt with one of these regularities; that is, with the law of definite proportions. This alone, however, would not have sufficed for that theoretical conception, and another law was also necessary, namely, the law of multiple proportions. The latter was propounded by Dalton in 1804, that is to say, prior to the close of the controversy regarding the constancy of the proportions by weight in which substances combine. I have intentionally departed from the chronological sequence of the facts, in order to secure their logical arrangement. The law of multiple proportions has no meaning, so long as the law of constant proportions is not proved. It includes the latter within it, and can only stand along with it. We may well be surprised that it should have been propounded at the very time when doubts were entertained as to the accuracy of the law of constant proportions. The explanation probably lies in the fact that Berthollet and Proust lived in France, whereas Dalton made his discovery in England, and withheld the publication of his investigations until 1808; whilst prior to that date the scientific world only obtained a short statement of the results of Dalton's experiments from Thomson's System of Chemistry, in which the investigations are mentioned. Dalton's theory, which very soon gained favour, undoubtedly exercised a decisive influence on the views of the chemists of the period with respect to constant proportions; and it is partly to be attributed to the labours of Richter, of Dalton, and of Wollaston, that Berthollet, if he did not exactly withdraw his previous assertions, at least did not further endeavour to bring about their acceptance.

It may be that Dalton, as his biographer, Smith, asserts,[1] had no knowledge, or only a very incomplete knowledge, of the work of Richter, which might otherwise have contributed materially to the establishment of the atomic theory.

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[1] Memoir of John Dalton and History of the Atomic Theory, 214.

He may have arrived quite independently at those ideas which exercised the greatest influence upon the subsequent development of chemistry, but we must here take notice of all the facts which are of importance in this connection, and we must not overlook Dalton's predecessors. Almost simultaneously with the conception of the atom, that of the equivalent was also developed. The recognition of the latter contributed to procure admission and general favour for the atomic theory, and it is therefore advisable, in my opinion, to deal with both ideas side by side as they arose chronologically. In doing so, it will be observed that Dalton's atom was introduced independently of the equivalent, but that Wollaston, in particular, endeavoured to replace the atom by the equivalent. This afterwards led to the identification of the two ideas, a fact which had a detrimental effect upon the science.

The first experiments which could have led to the establishment of equivalent quantities, were carried out by Bergman in the second half of the eighteenth century.[2] Bergman observed that neutral solutions of metals were precipitated by other metals, without the production of an acid reaction and without the evolution of gas. As an adherent of the phlogiston theory, he explains the observations quite correctly in accordance with the principles of the theory. He assumes that the precipitated metal has taken up just as much phlogiston as the precipitating metal has parted with; and in consequence of this view, he perceives a means of determining the quantities of phlogiston contained in different metals. The quantities of the dissolved and of the precipitated metals respectively, must stand to each other inversely as the supposed quantities of phlogiston contained in equal weights of these metals.

Lavoisier, who repeats and extends Bergman's experiments a few years afterwards,[3] recognises that they must show, in terms of his theory, the quantities of oxygen which combine with equal weights of the metals. Where Bergman had spoken of the taking up of phlogiston, Lavoisier only needs to assume the giving up of oxygen, and *vice versa :* the inverse ratio of the quantities of the precipitated metal A and of the dissolved one B gives Lavoisier the relations of the quantities of oxygen combining with equal weights of A and B; or otherwise, and more clearly expressed, the quantities of the precipitated and of the dissolved metal respectively, which the experiment furnishes directly, have the property of being able to combine with the same quantity of oxygen. The generalisation, in the latter form, was not emphasised, however, either by Bergman or by Lavoisier, otherwise it would probably have led to the notion of equivalence. This result did not follow, and even the experiments of both these chemists were but little heeded. It did not fare much better with the investigations of Richter, which were carried out between 1791 and 1802, and were supported by far more observations. Richter was the first to state the law of neutrality, and to deduce accurate conclusions from it.[4] This merit was formerly attributed erroneously to Wenzel, who arrived, however, at exactly the opposite result. The error which passed into many of the older text-books appears to have been caused by Berzelius,[5] and was pointed out by Smith,[6] and others.[7] On the other hand, the merit of having first stated a fundamental proposition of the doctrine of affinity belongs to Wenzel. (See note 94, p. 315.)

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[2] Bergman, Physical and Chemical Essays. Translated by E. Cullen, M.D., 2 (1784), 349 *et seq.* [3] Lavoisier, Oeuvres. 2, 528.

Richter observed that upon mixing solutions of two neutral salts, the neutrality is maintained, even when double decomposition takes place, and from this he concluded that the quantities a and b of two bases, both of which are neutralised by the same quantity c of an acid, are both likewise neutralised by the same quantity d of another acid ; and, conversely, that the weights of two acids which are neutralised by the same quantity a of a base, require for neutralisation the same quantity b of another base. The mode of expressing this which Richter employs is remarkable. He says :—[8]

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[4] Richter, Ueber die neueren Gegenstände der Chemie.

[5] Berzelius, Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'Électricité, Paris (1819), 2.

[6] Memoir of John Dalton, etc., 160.

[7] Wenzel determined the proportions in which base and acid combine to form salts. He found, however, exactly the opposite of what Berzelius makes him say. Compare Wenzel, Ueber die Verwandtschaft der Körper, Dresden (1782), especially 450 *et seq.*

"If P is the mass of a determining element, where the masses of the elements determined by it are a, b, c, d, e, etc., and Q is the mass of another determining element, where the masses of the elements determined by it are α, β, γ, δ, ϵ, and so on, but where a and α, b and β, c and γ, d and δ, e and ϵ, in each case represent one element, and the neutral masses $P+a$ and $Q+\beta$; $P+b$ and $Q+\gamma$; $P+c$ and $Q+\alpha$; $P+a$ and $Q+\gamma$, and so on, decompose by double affinity in such a way that the products obtained are again neutral, then the masses a, b, c, d, e, etc., have exactly the same quantitative ratio amongst themselves as the masses α, β, γ, δ, ϵ, etc., and conversely."

I must observe that by the determining element, and the element determined, Richter understood the quantities of acid and of base that mutually neutralise each other. Richter well understood the importance of the foregoing statement. He remarks :[9] "This rule is a true touchstone of the experiments instituted with regard to the relations of neutrality ; for, if the proportions ascertained empirically are not of the nature that the law of decomposition by double affinity requires, where the decomposition actually taking place is accompanied by unaltered neutrality, they are to be discarded as incorrect without further examination, since an error has then occurred in the experiments tried."

Richter tabulated the quantities of the bases which are neutralised by the same weight of sulphuric acid, of hydrofluoric acid, etc., and these he calls neutrality series, or series of masses ;[10] he also determined the quantities of the acids which are saturated by the same quantity of different bases.[11] In doing this, he thought he had discovered certain regularities, but this subsequently proved to be fallacious. Thus, according to him, the series of masses in the case of the bases formed an arithmetical, and that in the case of the acids, a geometrical series. He wished, in fact, to establish a regularity in chemical compounds, such as had been assumed in the distances of the planets from the sun, and, in order to accomplish this, he had probably corrected many of his results.

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[8] Neuere Gegenstände (1795). 4, 67. [9] Ibid. 4, 69. [10] Ibid. 4, 70. [11] Ibid. 4, 92 ; 6, 176.

Another department of Richter's "stöchiometric investigations" must be mentioned here; that is, his work upon metallic precipitations. He determines the quantities of the metals as they mutually precipitate one another from their solutions, and employs the numbers obtained to ascertain the proportion of oxygen in the oxides. Here again, his way of expressing himself leaves much to be desired. He says:—[12]

"When an aqueous solution of a metallic neutral salt is so decomposed by an inflammable metallic substrate, that is, by another metal in the metallic state, that not only does the metal which was dissolved separate out in a wholly metallic state, but also that neither the dissolving acid solvent nor the water associated with it, is decomposed, then the masses of the vital air which must unite with equal masses of the metallic substrates, in order to make their solution in acids possible, are inversely proportional to the masses (or weights) of the separating and of the separated metallic substrates from the metallic neutral salts." And at another place:—[13] "The quantitative order of the specific neutrality of the metals towards vitriolic acid does not by any means follow the usual order in which one metal is separated by another from the solution in the acid; on the contrary, it is wholly analogous to the inverse quantitative order of the removal of the inflammable matter and of the respective combination with vital air."

It is worthy of mention that Richter introduced the name Stöchiometry, which signifies the measurement of the proportions in which substances combine.

Fischer, on the other hand, deserves credit for having combined Richter's various tables into a single one. In this connection, he expresses himself as follows:—[14] "It is only necessary to determine the proportional quantities of one acid against the different alkaline bases ; afterwards, it is sufficient to ascertain the proportional quantity of a single compound of every other acid with one alkaline basis, when, by means of an easy calculation, the proportional quantities of the acids in all the other compounds may be determined." It may be said, indeed, that Fischer's table was the first table of equivalents. The numbers attached in it to the different bases, represent equivalent quantities, since these quantities are neutralised by the same quantity of acid ; and conversely with respect to the different acids. The conception of the equivalent was, in this way, established about the year 1803, although the word itself was not in use at that time. The discovery of the law of multiple proportions, and the formulation of the atomic theory by Dalton (which were first announced in the third edition of Thomson's System of Chemistry), both took place almost at this same time.

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[12] Neuere Gegenstände. **8**, 83. [13] Ibid. **8**, 127. [14] Berthollet, Statique Chimique. German translation with explanatory comments by Fischer, **1**, 135.

I wish to deal, in a few words, with the questions of priority which were called forth by these important experiments and views.[15] The idea of the atomistic point of view is an old one, and at the beginning of this lecture I have named a few Greek philosophers who advanced and upheld the theory. The opinions pass down through all the centuries ; they are contested ; but they always find supporters. The chemists of the eighteenth century appear to have embraced pretty generally the atomistic way of regarding matter. I may here adduce the views of Lavoisier with respect to the constitution of matter, which I have already stated at length ; and those of Berthollet, who frequently speaks of molecules. In one word, these were the opinions of the day, and they were preferred to the dynamic hypothesis, chiefly, it is almost certain, because the assumption of discreet particles of matter, separate from one another, furnished a simple explanation of the diminution of volume with the lowering of temperature.

Dalton, on his part, did not claim that he had introduced these opinions into the science. In this connection he says that the observation of the existence of different states of aggregation has "led to the conclusion which seems universally adopted, that all bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms of matter bound together by a force of attraction, which is more or less powerful according to circumstances, and which as it endeavours to prevent their separation, is very properly called in that view, *attraction of cohesion*."[16] And with regard to the "agency of heat" he says:—"An atmosphere of this subtile fluid constantly surrounds the atoms of all bodies, and prevents them from being drawn into actual contact."[17]

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[15] Compare the work by Smith, already mentioned.

Dalton shows, however, in the course of his most interesting work how the relative weights of these particles can be ascertained; and it will remain as his imperishable merit to have shown the possibility of determining the atomic weights. Higgins, it is true, tried to prove that he also participated in this important discovery;[18] but even if it must be admitted that Higgins employed the atomic theory as early as 1789,[19] still his way of expressing himself is not, by a long way, so clear and definite as Dalton's, and, so far as I know, he does not mention atomic weights.

Dalton turned the atomic hypothesis to account as the basis of chemical considerations, after he had found that when two substances unite in several proportions, these proportions are always expressible in simple multiples by whole numbers. He examined the two hydrocarbons, marsh gas and ethylene, and found that, for the same weight of hydrogen, there was twice as much carbon combined with it in ethylene as in marsh gas. He then examined to see whether any such regularity was to be found in other compounds, employing in particular for this purpose the oxides of nitrogen, and he thereby obtained confirmation of the law. The law is to this effect:—If two substances, *A* and *B*, form several compounds, of which the compositions are all calculated with respect to the same quantity of *A*, then the quantities of *B* combined with this, stand to each other in a simple ratio.[20] Dalton sought in the atomic theory an explanation of this law, which was simply an expression of the observed facts.

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[16] Dalton, A new System of Chemical Philosophy, 1, 141-142; Alembic Club Reprints, 2, 27. [17] New System. 1, 143-144. [18] Experiments and Observations on the Atomic Theory, by W. Higgins (1814). [19] A Comparative View of the Phlogistic and Antiphlogistic Theories,

According to the atomic theory, chemical compounds are formed by the arrangement, in juxtaposition, of atoms of the elements, these latter being incapable of undergoing any further decomposition. With regard to this Dalton says:—[21] "Chemical analysis and synthesis go no further than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency." By the fact that Dalton assigns a definite unalterable weight to the atom of every element, and admits the possibility of the combination of several atoms, his theory is brought into harmony with experiment, and becomes, indeed, a necessary consequence of it. According to the number of atoms which enter into combination, the resulting atom may belong to a different order.

The atoms of elements are simple atoms, or atoms of the first order.

When 1 atom of an element *A* combines with 1 atom of an element *B*, 1 atom of the second order is produced.

When 2 atoms of an element *A* combine with 1 atom of an element *B*, 1 atom of the third order is produced.

When 1 atom of an element *A* combines with 2 atoms of an element *B*, 1 atom of the third order is produced.

When 1 atom of an element *A* combines with 3 atoms of an element *B*, 1 atom of the fourth order is produced.

When 3 atoms of an element *A* combine with 1 atom of an element *B*, 1 atom of the fourth order is produced, etc.

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[20] It appears that Dalton never stated the law in this general form. Compare Memoirs of John Dalton, by W. Henry, 79 *et seq.*

[21] New System. **1**, 212; A.C.R. **2**, 29.

oxygen and nitrogen in the oxygen compounds of nitrogen.[24] He is acquainted with four of the latter. In nitric oxide he finds 7 parts of oxygen for 5 of nitrogen; its atom is, therefore, the atom of the second order, derived from these elements. In nitric acid, according to his view, there are 14 parts of oxygen for 5 of nitrogen, or two atoms of the former gas for one of the latter. In nitrous oxide, 7 parts of oxygen are combined with 10 parts of nitrogen, and in this he therefore assumes two atoms of nitrogen and one of oxygen. Nitrous acid, however, is supposed to contain 10½ parts of oxygen for 5 of nitrogen, and in it he might have assumed two atoms of nitrogen and three of oxygen. He prefers, however, to regard this substance as a compound of nitric acid and nitric oxide.

Further, he finds in ethylene 5.4 parts of carbon for 1 of hydrogen, and in marsh gas the same quantity of carbon for 2 of hydrogen. On this account, he regards ethylene as consisting of atoms of the second order, and assumes the atomic weight of carbon to be 5.4. Carbonic oxide likewise consists of atoms of the second order, since he finds in it 7 parts of oxygen for 5.4 of carbon, while carbonic anhydride has atoms of the third order, because it contains 14 parts of oxygen for 5.4 of carbon.

But Dalton does not always adhere quite rigidly to his own rules. Thus he regards sulphuretted hydrogen as consisting of one atom of sulphur and three of hydrogen, and sulphuric acid, of one atom of sulphur and three of oxygen, whereby he is led to 13 as the atomic weight of sulphur.

Hence there is, in my opinion, something haphazard in these atomic weight determinations, quite apart from the rules themselves. I shall return afterwards to the question whether the latter are justifiable or not. The numbers advanced by Dalton were thus relative in a twofold manner, if I may so express myself; they were affected by two unknown constants. In the first place they were all determined with reference to an arbitrary standard, and in the second, they were only relatively accurate with respect to this standard. The atomic weight of carbon had in reality only been found to be a *multiple* or a *submultiple* of 5.4. Dalton himself does not appear to have been aware of this arbitrary character of his numbers.

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[24] New System. 1, 215; A.C.R. **2**, 30-31.

In spite of this, his theory met with very general recognition, and chemists were astonished at the simplicity with which it explained all the regularities which had been discovered immediately before. With the rapid progress that the science was at that time making, some new support was necessary. In order to avoid being left behind it was essential to possess a general point of view from which the isolated facts and the different regularities could be conveniently surveyed. It was soon to be shown that this theory was capable of standing the test; that it was not only sufficient to connect the known phenomena, but that laws which were only discovered subsequently could also be explained by means of it. This holds especially for the law of gaseous volumes, which Gay-Lussac discovered in 1808, a few months after the appearance of Dalton's ingenious book.

As early as 1805, Humboldt and Gay-Lussac, on the occasion of their joint investigation of the composition of the air, had determined anew the proportions by volume in which hydrogen and oxygen combine.[25] They found slight differences from the earlier observations, and arrived at the highly interesting result that water is produced by the condensation of 2 volumes of hydrogen and 1 of oxygen; while Meusnier and Lavoisier[26] had found 23 volumes of hydrogen and 12 of oxygen, and Fourcroy, Vauquelin, and Seguin[27] had found 205.2 of hydrogen for 100 of oxygen.

Three years later, Gay-Lussac extended his experiments to other gases.[28] He had previously observed the law (often called after him) of the uniform expansion of gases with increase of temperature.[29] He was also familiar with the so-called law of Mariotte, which was discovered by Boyle, and which states the relation between pressure and volume; in short, he possessed all the data for reducing the results directly obtained to like pressure and temperature—a basis upon which to execute the experiments he had in view. His investigation is a model of accuracy, and, in this respect, it is very markedly distinguished from other experimental investigations of the period. The results obtained are extremely simple; and he states them somewhat after this manner. Two gases always combine in simple proportions by volume, and the contraction which they undergo, and, therefore, also the volume of the product formed, stand in the simplest relation to the volumes of the constituents.

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[25] Journ. de Phys. **60**, 129. [26] Lavoisier, Oeuvres. **2**, 360. [27] Ann. Chim. **8**, 230; **9**, 30. [28] Mém. d'Arcueil. **2**, 207. [29] Ann. Chim. **43**, 137.

Thus Gay-Lussac found, for example, that 2 volumes of carbonic anhydride are produced from 2 volumes of carbonic oxide and 1 of oxygen; that 2 volumes of nitrous oxide are composed of 2 volumes of nitrogen and 1 of oxygen; that equal volumes of nitrogen and of oxygen are combined in nitric oxide, while the product has the same volume as the two constituent gases separately; and finally, that 1 volume of nitrogen and 3 of hydrogen are condensed to 2 volumes in ammonia.

Gay-Lussac, who was well acquainted with Dalton's theory, shows at the end of his paper that the facts ascertained by him are in harmony with the theory; that, by the assumption of a similar molecular condition in all gases, it will explain their analogous behaviour towards changes of pressure and of temperature; and that his law of gaseous volumes is an important support of Dalton's view.

It might be supposed that the latter would have been highly pleased by so unexpectedly brilliant a confirmation of his views. This was not so, however. In the second part of his "New System of Chemical Philosophy," which appeared in 1810, he practically regards Gay-Lussac's experiments as erroneous. I shall endeavour to explain the reasons that prompted him to do this, especially as it has been stated that Dalton wished, from jealousy or want of judgment, to dispute Gay-Lussac's merits.

In the first part of his book, Dalton had already speculated as to the volume relations of the gases. He says there :—[30] "In prosecuting my enquiries into the nature of elastic fluids, I soon perceived it was necessary, if possible, to ascertain whether the atoms or ultimate particles of the different gases are of the same size or volume in like circumstances of temperature and pressure. By the size or volume of an ultimate particle, I mean in this place, the space it occupies in the state of a pure elastic fluid; in this sense the bulk of the particle signifies the bulk of the supposed impenetrable nucleus, together with that of its surrounding repulsive atmosphere of heat. At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous." He afterwards became of a different opinion, to which he was led by the following considerations :—One atom of nitric oxide consists of one atom of nitrogen and one of oxygen. If, now, there were the same number of atoms in equal volumes, one volume of nitric oxide should be formed by the combination of one volume of nitrogen with one of oxygen, but, according to Henry's experiments, about two volumes are produced; hence nitric oxide could only contain half as many atoms in the same space as nitrogen or oxygen.[31]

Dalton, in his reply, refers to these considerations, and then, with regard to Gay-Lussac's "hypothesis that all elastic fluids combine in equal measures, or in measures that have some simple relation one to another," he proceeds :—[32] "In fact, his notion of measures is analogous to mine of atoms; and if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, etc., the two hypotheses would be the same, except that mine is universal, and his applies only to elastic fluids. Gay-Lussac could not but see that a similar hypothesis had been entertained by me, and abandoned as untenable."

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[30] New System. 1, 187-188; A.C.R. 4, 6, 7. [31] Compare New System, 1, 70-71; A.C.R. 4, 5. [32] New System. 2, 556; A.C.R. 4, 25.

Dalton shows, moreover, the poor agreement between the results of Gay-Lussac and those of Henry, and this confirms him in his conclusion that the former had not observed accurately. It cannot be denied that Dalton's contention is well founded. If the atomic theory was chosen as the basis for chemical speculation, the law of gaseous volumes, as Gay-Lussac stated it, could only be brought into harmony with it if the assumption were admissible that equal numbers of the smallest particles are present in the same volumes of all gases. This assumption agreed with the physical properties of gases, but was, as Dalton quite rightly concluded from known facts, impossible. The three rules adopted by Dalton likewise told against the accuracy of this hypothesis. In water, for example, it would have been necessary to assume two atoms of hydrogen for one of oxygen; and it may be that this was also a reason for Dalton's coming forward so decidedly in opposition to Gay-Lussac.

It will be clear from these explanations that there was a real difficulty in bringing Gay-Lussac's law into harmony with the atomic theory. Avogadro was the first to show how this difficulty can be got over.[33] The Italian physicist distinguishes *molécules intégrantes* and *molécules élémentaires*, which, for brevity and simplicity, we shall translate by molecule and atom respectively. As a step towards the explanation of the observed facts regarding the proportions by volume in which gaseous substances combine with one another and of the relation of these proportions to the volume of the products, to which Gay-Lussac's law gives expression, Avogadro advances the hypothesis that equal volumes of all gases, whether elementary or compound, contain the same number of molecules. These molecules are not supposed, however, to constitute the ultimate particles of matter, but are assumed to be capable of further subdivision under the influence of chemical forces. According to Avogadro, therefore, substances (elements and compounds alike) are not converted, in passing into the gaseous state, into indivisible particles, but only into *molécules intégrantes*, which in turn are composed of *molécules élémentaires*. He bases his view upon the following considerations:—If nitric oxide, which arises without contraction from equal volumes of nitrogen and oxygen, contains as many molecules as the mixed gases do, then the combination cannot consist in the union with one another of previously separate molecules, since this would necessarily involve a diminution in the number of particles; but it must be brought about by an exchange. The molecules both of nitrogen and of oxygen must split into two parts, and these then combine by mutual exchange.

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[33] Journ. de Phys. 73, 58; A.C.R. 4, 28.

While, therefore, before the combination, the gaseous mixture consists of dissimilar molecules, of which the one half are composed of two atoms of nitrogen, and the other half of two atoms of oxygen, the product of the combination consists of the same number of molecules, but they are all like molecules and each has been formed by the union of one atom of nitrogen with one of oxygen. Consideration of the volume relations in the formation of ammonia, likewise points to a subdivision of the gas particles of elementary substances. All these discussions assume the simplest character when the word molecule (*molécule intégrante*) is employed instead of volume, the two conceptions being identical for the gaseous state, according to Avogadro's definition. From Gay-Lussac's numbers, then, it appears that the molecule of ammonia consists of half a molecule of nitrogen and one and a half molecules of hydrogen; that the molecule of water contains half a molecule of oxygen and one molecule of hydrogen, etc. If the simplest hypothesis with respect to the divisibility of the molecule is adopted, so that it is not necessary to introduce fractions of atoms, then the molecules, not only of hydrogen, but also of oxygen and of nitrogen, must consist of two elementary atoms; and the proportions, by volume, in which the gases combine, then give the number of chemical smallest particles which go to form the molecule. Avogadro finds, for example, that two atoms of hydrogen and one of oxygen are necessary for the formation of water; that three atoms of the former gas and one of nitrogen are present in ammonia, etc., and he thus arrives at results quite different from those of Dalton.

He points this out explicitly in his paper, and draws attention to the fact that in his determinations, he starts from legitimate physical principles, whereas Dalton's rules contained arbitrary assumptions. He lays stress on the fact that Dalton, in case he wishes to identify the physical with the chemical atoms (*molécules intégrantes* and *élémentaires*), will be forced to assume that in those combinations which take place without contraction, the composite atoms must be further removed from one another than the uncombined ones.

Avogadro is able, from their densities, to determine directly the molecular weights of the elements known in the gaseous state. This, however, is not sufficient for him, and he also attempts the determination in the cases of other elements. Here, however, he has recourse to more or less doubtful hypotheses. He finds the atomic weight of carbon to be 11.3, and that of sulphur 31.3, referred to that of hydrogen assumed = 1; that is, he finds numbers which very nearly agree with those adopted at present. I shall not enter into the more minute details of this most interesting paper, and shall only remark further that Avogadro admits the possibility of molecules of elements consisting of 4, 8, etc., atoms, and believes that nature has, in this very way, equalised the difference between simple and compound substances.

Starting from similar views, Ampère writes a paper on the same subject three years later (1814).[84] His conclusions are, however, less simple, as he tries at the same time to explain the crystalline form of substances by the position of the atoms in the molecule.

These speculations met, on the whole, with but little attention in the chemical world. It seems as if a distinction between atom and molecule was not regarded as justifiable, and accordingly neither Avogadro's nor Ampère's ideas exercised any immediate influence upon the science. This may also be explained by the fact that the hypothesis only led to decisive results as to the number of atoms contained in the molecule (and thus to the determination of the atomic weight) in the case of gaseous substances, and was not applicable to solids and liquids. Chemists, therefore, looked for new generalisations, and the next impulse in this direction was given by Wollaston.

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[84] Ann. Chim. **90**, 43.

Wollaston had carried out an investigation on the carbonates, in 1808,[35] which appeared simultaneously with an examination of the oxalates by Thomson.[36] It was shown in the papers of these chemists that carbonic acid can form compounds with one and with two parts, and oxalic acid with one, with two, and with four parts of potash. These experiments produced a great impression, because at that time there were few facts of this kind known which had been minutely examined; on this account, they formed an important support to the law of multiple proportions. But if Wollaston, on the one hand, thus exerted an influence upon the rapid recognition which the atomic theory met with, and consequently came to be regarded even by authorities as an adherent of the theory,[37] still, by a later paper,[38] he contributed to the abandonment of the atom by a section of chemists, as too indefinite a basis for chemical considerations.

In 1814, Wollaston, not without justice, represents to Dalton how uncertain and arbitrary is his estimation of the number of atoms in a compound; and how, in consequence, the atomic weights are wholly hypothetical numbers, so that, in his opinion, they should not be adopted. He advised, instead of the conception of the atom, the introduction of the equivalent, which word he employs for the first time. Wollaston was well acquainted with Richter's works,[39] and he derives the conception of the equivalent principally from his investigations. I must at once remark, further, that, with him, not only are those quantities of two bases equivalent which are neutralised by the same quantity of acid, and those quantities of metal equivalent which mutually precipitate each other (and therefore unite with the same weight of oxygen), but that also, in his determinations, he extends far beyond these limits, without, it would appear, ever clearly perceiving that he falls into exactly the same error that he points out to Dalton. I go further, even, and assert that the uncertainty was increased by him, since he first employed the equivalent in the sense of the atom, and thereby attached to it the vague signification which remained connected with it; and so it was this very paper which principally led chemists to the fusion of the two conceptions, and thereby to the tacit and inaccurate assumption that the atoms were equivalent, an error which gave rise to great confusion.

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[35] Phil. Trans. 1808, 96; A.C.R. **2**, 34.

[36] Phil. Trans. 1808, 63; A.C.R. **2**, 41.

[37] Kopp, Geschichte. **2**, 373.

[38] Phil. Trans. 1814, 1; Ann. Chim. **90**, 138.

[39] Even Wollaston remarks (*loc. cit.*) that Wenzel's analyses do not agree with the law of neutrality.

I shall here give an example of Wollaston's determinations, so that the reader may obtain at least an idea of his method, and may satisfy himself as to the accuracy of my opinion. Wollaston sets out from the equivalent of oxygen, which he assumes = 10; from this he determines the equivalent of hydrogen to be 1.3, clearly because 1.3 parts of hydrogen (according to the estimations of the period) unite with 10 parts of oxygen to form water; thus equivalent quantities are, with Wollaston, the quantities in which substances combine. But how, we may ask, does he proceed in the cases of substances that combine in more than one proportion—in the case of carbon, for example? Does he recognise several equivalents here? The answer is, no, he never appears to think that such a thing can be possible. He adopts the equivalent of carbon as 7.5, determining it from that of carbonic anhydride, which, according to him, is 27.5. He does not give any reason, however, for choosing the latter number, and we are left to find it out for ourselves. We might suppose that Wollaston regarded as the equivalent that quantity of carbonic acid which saturates a quantity of a base containing 10 parts of oxygen, whereby he would necessarily have adhered to the view stated above, that the combining weight is identical with the equivalent. He is obliged, however, as a consequence from his own figures, to assume in carbonic acid, two equivalents of oxygen for one of carbon. In this case, therefore, the combining weight and the equivalent were no longer identical, but the one was twice as great as the other. That such results were unavoidable in his method, ought to have been clear to him at once, since he was acquainted with the law of multiple proportions. Wollaston does not, however, pause in the least on account of this result ; he does not bestow a word upon it ; and he continues his determinations of equivalents unconcernedly, but we shall not follow him in these, as they possess no further interest for us.

I think I have now shown that Wollaston's equivalents present the same uncertainties as Dalton's atomic weights, and that the views stated by him must be called retrograde because he believed that he was dealing only with real unambiguous conceptions, free from all hypotheses.

It may perhaps seem that the opinion stated here is severe and unjust, but when the further development of chemistry is followed up, and it is seen how a more rapid progress during the succeeding decade was prevented by this very confusion of equivalent and atom (or combining weight), and how a most vigorous struggle was necessary before the separation of the conceptions could be re-introduced, the reader will probably adopt my view. It is true that the blame does not rest with Wollaston alone, because a school arose in Germany also, probably stimulated by him, which represented the same ideas. This school was at first, no doubt, dominated by the great influence of Berzelius, but afterwards, especially at the beginning of the fifth decade of the nineteenth century, it took the lead itself. I do not intend to withhold the details of these highly interesting developments, but in the next lecture I must direct attention to the electrical phenomena which at this time begin to exercise a great influence upon our science.

LECTURE V.

DAVY'S ELECTRO-CHEMICAL THEORY—DISCOVERY OF THE ALKALI METALS—DISCUSSION REGARDING THEIR CONSTITUTION—DOES HYDROCHLORIC ACID CONTAIN OXYGEN?—HYDROGEN THEORY OF ACIDS.

IF we look back to the period when the alkalies were regarded as simple and undecomposable substances, we can easily understand the enthusiasm with which the chemical world greeted the discovery of potassium and sodium. We are all familiar with the remarkable properties of these elements—with their metallic appearance and low specific gravity, their changeability in the air, their easy inflammability upon water, etc. It can be understood, therefore, that when substances possessing such properties had once been seen, illusions of all kinds were entertained by some people. The idea was arrived at that the substances hitherto known were only compounds, and that the aim of chemistry was now to discover the true elements, which, it was supposed, would resemble potassium and sodium. It is likewise comprehensible why the agency which had accomplished such results should be admired and overestimated. Everything was supposed to be possible by means of it, and the direction which chemistry would necessarily follow—that of electro-chemical development—was clear to every one. The galvanic current, at that period an entirely new agent, had accomplished this marvel, and it was itself a marvellous thing. By its aid it had become possible to decompose compounds into their true elements; hence it is not surprising that this agency was regarded as identical with the one which gave rise to combinations, *i.e.*, with affinity. It was believed that an explanation was thereby furnished for two things, both of which stood in need of it—that is to say, for electrical and for chemical phenomena, and the connection between these two was now shown. The further development of the electro-chemical theories appeared at that time to be the highest aim of our science ; at a later date we see these theories abandoned. The extraordinary enthusiasm was succeeded by an indifference just as extraordinary. In those cases where it was formerly believed (as regards the structure of the most complicated compounds) that the real secrets of nature were being discovered, the ordinary phenomena of decomposition were afterwards recognised. A secondary importance only, was usually ascribed to the latter in determining the constitution of substances. The electrical properties of substances, which at that time also indicated their position in the system, afterwards became of less consequence in the determination of their chemical character.

This is just such an example as is met with in the history of every science. Some great end is achieved, in comparison with which everything else becomes dwarfed into insignificance. Every endeavour is turned towards development in the new direction, and a system is established which has the observed phenomena for its basis. Then facts appear which are in conflict with the views that have thus arisen. These facts are a sufficient ground for some to abandon the theory ; but for others they act merely as a stimulus to bring the new experiments into harmony with the theory, and this compels them to have recourse to further hypotheses. In this way a controversy is developed which only ends when the supporters of the older view have their eyes opened so as to recognise how greatly the originally simple and elegant theory has been disfigured. The whole system now falls to pieces, and it is no longer comprehensible how any one could have permitted himself to be guided by such views. The greatest folly is now perceived in what had been previously recognised as the highest wisdom. So the times change !

The electro-chemical theories had the same fate. If we consider the astonishing discoveries which were made by means of the galvanic current, we can understand the importance which attached at that time to electrical phenomena ; and I believe I may almost assume that we would do similarly if we were placed in the same position. Listen, and judge!

In 1789 Galvani[1] discovered that upon simultaneously touching a muscle and a nerve of a frog, by means of two different metals which were joined together by a conductor, the frog was convulsed. Galvani's explanation of this fact was controverted and replaced by another, in 1792, by Volta.[2] We find the question of the cause of the electrical current discussed for a long period. Is the contact of the two metals sufficient to generate electricity, or must they also be separated by a decomposable fluid conductor? The reader is, no doubt, aware of the answer which we must now give to this question, in accordance with our scientific principles, even although the opposite view is perhaps not wholly refuted.[3] We cannot in this place further occupy our attention with these theories, which belong to physics, and not to chemistry.

Nicholson and Carlisle[4] observed in 1800, that upon discharging the galvanic pile through water, the latter is decomposed into its constituents, hydrogen and oxygen. Many endeavours were made to observe similar phenomena in the cases of other substances, but the first of the more important investigations into the nature of the decomposition of chemical compounds by means of the electric current comes from Berzelius and Hisinger, and was published in 1803.[5] These two investigators studied the action of dynamic electricity upon salt solutions, and, further, upon ammonia, sulphuric acid, etc. Their apparatus was so arranged that they were able to collect, separately, the constituents liberated at the different poles. In this way they arrived at the highly remarkable result, that substances may be divided into two groups in respect to their behaviour towards the galvanic current; that hydrogen, the metals, the metallic oxides, the alkalies, the earths, etc., separate at the negative pole of the battery, while oxygen, the acids, etc., separate at the positive pole. Besides this, they believed that they had discovered relations between the quantities of the substances decomposed, their mutual affinities, and the quantities of electricity derived from the battery.

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[1] De Viribus Electricitatis in Motu Musculari Commentarius. Commentarii Acad. Bononiae. Vol. **7** (1791). [2] Giornale Fisico-medico di L. Brugnatelli, 1794; Gren's Journal der Physik. [2], **2**. [3] Compare Wiedemann, Galvanismus. **1**, 25. [4] Nicholson's Journal (quarto), **4** (1801), 183. [5] Ann. Chim. **51**, 167.

With respect to the cause of the decomposition, they only express themselves in a very uncertain manner; they believe that this decomposition may be explained by the greater or less attraction that the electricity exerts upon the different substances.

I now turn to Humphry Davy's investigations, which, as he says himself, were begun in 1800.[6] He commenced them with, apparently, a quite unimportant question. Even in the first experiments on the decomposition of water[7] it was believed that the formation of alkaline and of acid substances as products of the electrolysis had been observed. Cruickshank[8] and Brugnatelli[9] confirmed this observation, and a belief was entertained in the conversion of water into alkalies and acids under the influence of the electricity. Simon[10] had already opposed this view, and Davy refuted it by decisive experiments.[11]

Davy causes the decomposition to take place in vessels made of different materials—glass, agate, gold, etc.—and satisfies himself that the nature and quantity of the substances liberated are thereby varied. This leads him to the assumption of the decomposition of the vessel. But even when he carries out the decomposition in gold vessels, he observes the formation of the volatile alkali (ammonia) and of nitric acid. These, he now concludes, owe their formation to the air (nitrogen) which was dissolved in the water. In order to satisfy himself of the accuracy of this view, he causes the decomposition to take place in closed vessels, pumping out the air which is in contact with the surface of the water, and substituting for it an atmosphere of hydrogen. In this way he succeeds in proving that pure water is decomposed by the action of the electric current into its constituents, hydrogen and oxygen, but that no other kind of change occurs in the water; and that all observations of the apparent occurrence of such change are to be explained either by some action upon the vessel in which the experiment has been conducted, or by some impurity in the water.

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[6] Phil. Trans. 1807, 2. [7] Nicholson's Journal (quarto), 4 (1801), 183. [8] Ibid. 188-189. [9] Phil. Mag. 9, 181. [10] Gilb. Ann. 8 (1801), 36. [11] Bakerian Lecture for 1806 (Phil. Trans. 1807, 1).

This enquiry is comparable, in many respects, with the first of Lavoisier's investigations.[12] In both cases an endeavour is made to refute a statement based upon inaccurate observation, and that not simply by speculation, or by the assertion that it is in contradiction to general views. In opposition to the earlier superficial experiments, new ones are adduced which have been carried out with the most minute attention to all the conditions. In both cases the purpose is attained, and the older inaccurate view is replaced by a correct one. Such results as those obtained in these cases by Lavoisier and by Davy are often called negative, but most people will agree with me when I assert that they may be of great positive value.

Davy, however, does not stop here. He next investigates the decomposition of salt solutions, and finds confirmation of the statements of Berzelius and Hisinger. But he proceeds with still greater circumspection, and endeavours to follow up the phenomena more exactly. All the means are at his command, and he does not fail to avail himself of them.

Direct observation shows Davy that hydrogen, the alkalies, the metals, etc., are separated by means of the current at the negative pole, and oxygen and the acids at the positive pole. From this he concludes that the former substances possess a positive, while oxygen and the acids possess a negative electrical energy; that in this case, as usual, the oppositely electrified bodies attract each other; and that, in consequence, the positive substances separate at the negative pole, and *vice versa*. In this assumption Davy had arrived at a conception, or, shall I say, an explanation of the phenomena of decomposition observed in the galvanic circuit. But he goes a step further, and tries to refer all chemical combination and decomposition to similar causes.

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[12] See p. 22.

Volta had assumed[13] that simple contact of two heterogeneous bodies was sufficient to place them in opposite electrical conditions, and this hypothesis explained the generation of the electric current to himself and to his numerous followers. Davy identified himself with this opinion, and tried to prove its accuracy by direct experiments.[14] He brought dry, insulated acids into contact with metals, and showed by means of the gold-leaf electroscope that the acids thereby become negatively, and the metals positively, electrified. He observed similar phenomena on rubbing sulphur upon copper, when the former became negative and the latter positive. Davy found further that these electrical energies which, in the last case, for instance, are only slight at ordinary temperatures, increase considerably on heating, and are very great at the melting-point of sulphur. On still further elevating the temperature, the two substances unite with evolution of light, and the compound obtained is non-electric. Davy concludes from this that the combination consists in a mutual discharge of the opposite electricities, and that heat and light, which appear simultaneously, are consequences of this discharge. According to him, chemical affinity is produced by difference in electrical condition, and the affinity increases or diminishes the greater or less this difference is. In cases where there is considerable difference of energy, equalisation is accompanied by phenomena of fire; with feebly electrified substances, only small quantities of heat are evolved; but if combination is to take place at all, the electrical energy must always be able to overcome the cohesion of the substances. Davy tries to prove directly the dependence of chemical affinity upon electrical condition, since he says:—[15]

"As the chemical attraction between two bodies seems to be destroyed by giving one of them an electrical state different from that which it naturally possesses; that is, by bringing it artificially into a state similar to the other, so it may be increased by exalting its natural energy. Thus, whilst zinc, one of the most oxidable of the metals, is incapable of combining with oxygen when negatively electrified in the circuit, even by a feeble power; silver, one of the least oxidable, easily unites to it when positively electrified; and the same thing might be said of other metals."

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[13] Brugnatelli, Ann. di. Chim. **13** and **14**; compare also Ann. Chim. 40, 225. [14] Phil. Trans. 1807, 32. [15] Ibid. 1807, 39.

He observes in another place that if there were no cohesion, the chemical attraction would necessarily be proportional to the electrical forces. Both are, in his view, effects of the same power, which, if it extends to the mass of a substance, gives rise to electricity, while, if it excites the smallest particles, it produces affinity.[16] By the action of the electric current, the electricity which was liberated from the atoms upon their combination, is restored to them again, and decomposition is thereby effected. In this action the positive substance goes to the negative pole and *vice versa*.

It must be admitted that these views start from a simple and a clear idea, and that by the application of this idea they explain the observed facts in a way that is easily understood. They therefore fulfil the conditions which are required in a scientific hypothesis, and secure that their founder, Davy, shall always be regarded as an investigator of undoubted originality. Davy's fame spread very rapidly, and, when he succeeded, a year afterwards, in isolating the alkali metals, it appeared as if he had, for the first time, pointed out the proper line of advance in chemistry. It is true that Davy's theory was illuminated by but short glimpses of sunshine, for ten years later we find that it is abandoned. It was certain to fall as soon as the contact with one another of heterogeneous substances was no longer regarded as a source of the excitation of electricity; and the affirmative view with respect to this matter was soon vigorously contested. Ritter, in particular, strove to show[17] that galvanic currents are only produced simultaneously with the occurrence of chemical decompositions. He assumed that electrical phenomena are the consequences of chemical processes, but that mere contact is not sufficient to produce different electrical conditions.

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[16] Davy, Elements of Chemical Philosophy, 165.

[17] Ritter, Elektrisches System, 49; see also Gehlert's Physikalisches Wörterbuch. 4, 795.

Davy's theory could not be brought into harmony with these views, and accordingly it was given up. This was not, however, on chemical but on physical grounds. A new system had in fact already arisen, which was able effectively to take the place of the old one. This was the electro-chemical theory of Berzelius. I postpone its discussion until the next lecture, because otherwise I should require to enter fully into the researches of Berzelius; whereas I desire at this place to explain more clearly the influence of Davy upon chemistry, by giving some account of the discovery of potassium and sodium, and of the discussion regarding the nature of these substances.

In the course of his investigations respecting the conversion of water into acid and basic substances, Davy had had opportunity of gaining a knowledge of the decomposing power of the electrical current, since neither glass, agate, nor felspar had proved able to resist its effects. He thus hit upon the idea of exposing the alkalies also to this action, in order to separate them into their constituents if any such were present in them.[18] For these experiments he first employs concentrated aqueous solutions of potassium and of sodium hydroxides; and as he does not succeed in obtaining products of their decomposition in this way, he next passes the current through the fused alkalies. He now observes the formation of small metallic globules, which burn, however, with great brilliancy, as soon as they come into contact with the air. Yet, by suitable arrangements, he succeeds in isolating small quantities of potassium and of sodium, and in studying their most important properties. I remark, in passing, that he only obtained potassium in the fused state. Gay-Lussac and Thenard, who showed how to effect the reduction of the alkali metals by means of iron, in 1808,[19] first proved that potassium is solid at ordinary temperatures. They used purer materials, and, by their method, they had much larger quantities of the new substances at their disposal.

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[18] Phil. Trans. 1808, 1; A.C.R. **6**, 5.

I cannot enter here into the complete history of potassium and sodium, although the subject becomes highly interesting from the facts that all Davy's experiments are at once checked by the French chemists; that the latter then bring forward independent results, which Davy doubts; and so forth. But one point in this somewhat vigorously sustained discussion seems to me to be of sufficient importance to deserve attention, namely, the views concerning the constitution of potassium and of sodium, and those concerning their relation to the alkalies.

In the decomposition of the alkalies, Davy had observed that the potassium and sodium appear at the negative pole, whilst oxygen is simultaneously evolved at the positive pole.[20] He had further found that the new substances possessed the property of reducing metallic oxides;[21] and he believed that the alkalies were reproduced when the metals were burned in oxygen.[22] From these results he draws the conclusions that the alkalies are the oxides of metals, and that the substances he has discovered are the metals themselves.[23] The physical properties of the substances, especially their metallic lustre, supported this view, although their low specific gravity seemed to be an argument, but not a sufficient one, against his conclusions. Davy accordingly proposes, for the substances, the names *Potassium* and *Sodium*, in which the termination is intended to indicate their metallic nature.

Davy now holds so firmly to this hypothesis regarding the constitution of the alkalies, that he also regards as oxides many other substances about whose composition the evidence is not yet by any means so clear. Thus, like his contemporaries, he assumes the existence of oxygen in hydrochloric acid, and, in opposition to the experiments of Berthollet,[24] advances the opinion that ammonia is also an oxygen compound.[25] He suspects the presence of oxygen in silicic acid, which he tries to reduce;[26] in the earths, which, as we know, he succeeded in reducing;[27] finally also in phosphorus and sulphur,[28] a view which was refuted by Gay-Lussac and Thenard.[29]

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[19] Ann. Chim. **65**, 325.

[20] Phil. Trans. 1808, 6; A.C.R. **6**, 10.

[21] Phil. Trans. 1808, 19; A.C.R. **6**, 22.

[22] Phil. Trans. 1808, 8; A.C.R. **6**, 11.

[23] Phil. Trans. 1808, 32; A.C.R. **6**, 34.

Some time afterwards, when engaged upon the investigation of ammonium amalgam[30] (which had been discovered shortly before by Seebeck[31] and more minutely studied by Berzelius and Pontin[32]), he finds its behaviour to be analogous to that of the other amalgams, and assumes that it is produced by the combination of mercury with a hypothetical substance, ammonium, resembling the metals and itself containing hydrogen and ammonia. In comparing now this ammonium with the metals, he is led to ascribe a similarity of constitution to both; that is, he assumes the existence of hydrogen in the metals also, whereby their combustibility could be explained. Davy states this as a possibility, which he most correctly recognises as identical with Cavendish's phlogiston theory, and which he naturally extends to potassium and sodium.

Gay-Lussac and Thenard arrived almost simultaneously at the same view.[33] They had investigated the action of potassium on ammonia gas, and, in doing so, had observed the formation of a green substance (potassamide), with simultaneous evolution of hydrogen. In these experiments, which they carried out quantitatively, they found the quantity of hydrogen evolved to be identical with that which the quantity of potassium employed would have liberated from water. They further showed that, in addition to the formation of potash, the whole of the ammonia employed was generated anew on the decomposition of the green substance by the action of water upon it. They explained these observations by the assumption that potassium consisted of potash and hydrogen; and that the latter was liberated by treatment with ammonia, as well as with water, the alkali combining simultaneously with the ammonia or with water. Thus, in accordance with their view, potassamide was composed of ammonia and potash, and it was decomposed into these constituents by the action of water upon it.

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[24] Mem. de l'Acad. 1785, 324; Stat. Chim. **2**, 280; E. **2**, 238.

[25] Phil. Trans. 1808, 35; A.C.R. **6**, 37.

[26] Phil. Trans. 1810, 59.

[27] Ibid. 1810, 16, 62, etc.

[28] Ibid. 1809, 67, etc.; Ann. Chim. **76**, 145.

[29] Recherches physico-chimiques, 1, 187.

[30] Phil. Trans. 1810, 37.

[31] Gehlen's Journal für die Chemie, etc., 5, 482.

[32] Bibliothèque Britannique (1809), 122, Nos. 323 and 324; Gilb. Ann. **36** (1810), 261.

[33] Ann. Chim. **66**, 205.

Davy, meanwhile, had reverted to his first explanation, and he now attacks these latest results obtained by Gay-Lussac and Thenard.[34] In so far as the accuracy of his experiments is concerned, however, he falls short of his opponents, although he is more fortunate and more masterly in the interpretation of them. In his view, the evolution of hydrogen during the action of potassium on ammonia, arises from the decomposition of the latter. According to him the green substance is composed of potassium and the residue from the ammonia gas. On treating the green substance with water, the latter is decomposed into its constituents, regenerating ammonia, and giving its oxygen to the potassium which is thus converted into potash.[35] In addition to this, since he considers fused caustic potash to be free from water, he finds in the conditions necessary for the preparation of potassium, a further argument against its containing hydrogen.

Gay-Lussac and Thenard persist, at first, in their previous opinion that potassium and sodium are hydrogen compounds,[36] and in this they are supported by the contemporaneous statements made by Berthollet[37] and by D'Arcet,[38] who regard fused potash as containing water. In 1811, however, they adopt Davy's view.[39] The reason for their change of opinion is to be found in the following facts. They had observed that the substance obtained upon burning potassium is different from potash, in so far that it contains more oxygen than the latter;[40] and they point out that the fact of potassium containing hydrogen would necessitate that the new oxide should contain water, since the production of uncombined water is not observed during the combustion. Further, as the oxide is decomposed by dry carbonic anhydride with the formation of oxygen and potassium carbonate, their hypothesis as to the composition of potassium leads to the assumption of the presence of water in salts, in cases where analysis does not reveal any.

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[34] Phil. Trans. 1808, 365 (Note). [35] Ann. Chim. **75**, 168 *et seq.*, 264. [36] Ibid. **75**, 299. [37] Mém. d'Arcueil. **2**, 53. [38] Ann. Chim. **68**, 175. [39] Rech. phys. chim. **2**, 250, etc.

From this period onwards the non-decomposability of the metals was no longer seriously doubted. At the same time the elementary nature of phosphorus and of sulphur was established anew by decisive experiments of Gay-Lussac and Thenard,[41] and the view that ammonia contained oxygen was recognised as an error by the younger Berthollet.[42]

To the foregoing, I may add an account of another scientific discussion, between Davy on the one hand, and Gay-Lussac and Thenard on the other, which is also of importance inasmuch as it led to the overthrow of Lavoisier's theory of acids. The discussion in question touches the composition of hydrochloric acid. In this acid, as in all others, Lavoisier had assumed the existence of oxygen. Its presence there had never been established, it is true, but the general theory required it; and as this theory was almost universally adopted, the existence of oxygen in hydrochloric acid seemed to be unquestionable. I say it was *almost* universally adopted, because Berthollet, for instance, was of a different opinion. In 1787 the latter had examined hydrocyanic acid, discovered some time previously by Scheele,[43] and had found in it carbon, hydrogen, and nitrogen only. It was likewise known, from other investigations by Scheele, that sulphuretted hydrogen contains hydrogen and sulphur only; and consequently Berthollet felt justified in regarding other elements as acid-producing, as well as oxygen.[44] He does not appear, however, to have had many adherents in this view, and, so far as hydrochloric acid is concerned, he also assumed the existence of oxygen in it. Chlorine was looked upon as oxygenated muriatic acid, and was supposed to be produced from muriatic (hydrochloric) acid by its taking up oxygen.

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[40] Rech. phys. chim. **1**, 125. [41] Ann. Chim. **73**, 229. [42] Mém. d'Arcueil. **2**, 268. [43] Ann. Chim. **1**, 30. [44] Stat. Chim. **2**, 8; E. **2**, 8.

These latter views were strengthened by the experiments of Henry, and by the interpretation of them which he gave.[45] He passed electric sparks through gaseous hydrochloric acid, which was confined over mercury, and obtained hydrogen, while the metal was simultaneously attacked by what he believed to be free oxygen. This led him to the assumption of the presence of water in hydrochloric acid, a view which found general approval since the investigations of others appeared to be in agreement with it.

In 1808, Davy had decomposed hydrochloric acid by means of potassium,[46] and in this way had obtained hydrogen and potassium chloride, the latter of which he had also prepared by burning potassium in chlorine. He showed, in 1809, that the chlorides (muriates) of the metals are not decomposed by heating them with phosphoric glass,[47] or with silicic anhydride, but that decomposition at once begins when aqueous vapour is passed over the mixture.[48] Davy was of opinion that Henry's hypothesis furnished the explanation of these experiments, and that hydrochloric acid could only be separated as soon as the quantity of water necessary for its existence was supplied. Gay-Lussac and Thenard further showed, about the same time, that water is produced as well as silver chloride by the action of this acid upon silver oxide; and, as formerly, they assumed that this water was already present in the hydrochloric acid.[49] They then effected the synthesis of the acid, by exposing a mixture of chlorine and hydrogen to sunlight.[50] On this occasion, they advance a complete theory regarding hydrochloric acid and chlorine, by means of which they are able to explain all their experiments.[51] According to them, hydrochloric acid is a compound of an unknown radical, *muriaticum*, with oxygen and water; chlorine, on the other hand, is anhydrous hydrochloric acid combined with more oxygen, or, what amounts to the same thing, it is ordinary hydrochloric acid minus hydrogen. On this hypothesis the above-mentioned experiment of the synthetic formation of hydrochloric acid is easily explained. The other facts connected with the matter can be explained on the same hypothesis in just as logical a manner. It is true that the two French philosophers exerted themselves fruitlessly in trying to give direct proof of the presence of the supposed oxygen. It was in vain that they passed hydrochloric acid gas over red-hot charcoal: no change was observable, and this negative result might well have led them to another explanation.[52] They point out that the hypothesis that chlorine (oxygenated muriatic acid) is a simple substance, and hydrochloric acid its hydrogen compound, could also serve as the basis for the explanation of the observed facts; they prefer, however, to adhere to the old view.

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[45] Phil. Trans. 1800, 191.

[46] Ibid. 1809, 91; A.C.R. **9**, 7.

[47] Phosphoric glass is calcium metaphosphate; obtained by sufficiently strongly heating monocalcium phosphate.

[48] Phil. Trans. 1809, 93; A.C.R. **9**, 9.

[49] Rech. phys. chim. **2**, 118.

[50] Ibid. **2**, 159.

Davy, who arrived, independently it would appear, at the latter assumption, declares himself a decided adherent of it.[53] He lays great stress on the fact that it agrees with Scheele's original idea, in accordance with which chlorine was dephlogisticated hydrochloric acid; and he tries to support this view by means of new arguments and new experiments. He draws attention to the fact that chlorine does not become converted into hydrochloric acid by the removal of oxygen, but only by treatment with substances containing hydrogen; and, further, that chlorine is a neutral substance, which, adopting the old hypothesis, is not in agreement with Lavoisier's theory, since it would then be necessary to assume that a substance indifferent to litmus had been obtained from an acid by the addition of oxygen to the latter. Finally, he points out to chemists the many hypothetical substances to which it is necessary to have recourse in order to preserve the older view, whereas the new one explains the facts in the simplest manner.

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[51] Mém. d'Arcueil. **2**, 339; Bulletin de la Soc. Philomatique, No. 18, May, 1809. [52] Mém. d'Arcueil. **2**, 357-358. [53] Ann. Chim. **76**, 112 and 129.

Gay-Lussac and Thenard do not admit this. In 1811, when they publish their investigations in full, under the title: *Recherches physico-chimiques*, they place the two theories side by side, and show how both suffice to explain the facts.[54] Nevertheless, they declare against the new system, and the reason they give for doing so, deserves to be mentioned. If chlorine were a simple substance, dry sodium chloride would necessarily decompose water when it dissolved in it, in order that muriate of soda might be produced; and this they consider more than unlikely. Moreover they held Lavoisier in too high esteem to abandon lightly any such doctrine as the one advanced by him that all acids contain oxygen.

But their resistance did not avail them long; the force of facts was stronger than they were, and Gay-Lussac was far too clear-headed a thinker to be blind to them. The facts that made him an adherent of Davy's view, in 1813, were especially his own experiments upon iodine,[55] which had been discovered by Courtois and described by Clément,[56] and whose analogy with chlorine he recognised and emphasised; and further, the discovery of hydriodic acid. From this time onwards, the new theory gains ground, and even Berzelius is unable to alter the current of opinion, although he puts himself to every conceivable pains, in a paper published in 1815, to deter chemists from the threatened step.[57] After pointing out that the hypothesis of *muriaticum* is still in a position to explain the facts, he draws attention to the fact that it, alone, is in agreement with the general theory of acids; whereas, on the assumption that there is no oxygen present in hydrochloric acid, a distinction is drawn between this compound and the other acids, to which, nevertheless, it shows the greatest resemblances. The salts also, would then necessarily fall into two classes; or in other words, it would be necessary to assume differences in constitution in a series of substances whose behaviour is similar in every respect. He thinks, further, that he is justified in concluding from the laws of combination, that chlorine is not an element. I do not enter more minutely into the matter since his arguments had little effect. They came too late. Gay-Lussac's investigation of hydrocyanic acid in the same year[58] indisputably proves the acid nature of this compound, and the fact that it does not contain oxygen; and hence even Berzelius cannot maintain Lavoisier's definition of the acids and of the acidifying principle.

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[54] Rech. phys. chim. **2**, 94. [55] Ann. Chim. **91**, 5. [56] Moniteur. 1813, Nos. 336 and 346. [57] Ann. Phil. **2**, 254; Schweigger's Journal. **14**. 66.

Some other cause which might furnish the acid character observed in certain substances was now sought for. The conception of an acid seemed so definite at that time, and the substances included in this class were so distinctly separated from all other substances, that it was necessary to enquire into the cause which occasioned this difference. Besides, it cannot be denied that Lavoisier, and even the chemists of the beginning of the nineteenth century were still influenced, in a certain respect, by the ideas of the Greek philosophers. Just as the latter ascribed general properties to the presence of a common constituent and identified the particular property to a certain extent with a particular constituent—just as they explained combustibility, for example, by the presence of a fire-material—so Lavoisier and his adherents believed that in oxygen they had discovered the acidifying principle.

In a similar manner we find Davy, after he was satisfied that hydrochloric acid contains hydrogen and chlorine only, stating the view that the chlorine is the acidifying principle in it, and the hydrogen its basis or radical.[59] At a later date Gay-Lussac[60] introduces the name "hydracids" for the acids free from oxygen, and places hydrochloric acid, hydrocyanic acid, sulphuretted hydrogen, and hydriodic acid in this class.

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[58] Ann. Chim. **95**, 136.

[59] Phil. Trans. 1810, 231; A.C.R. **9**, 21.

[60] Ann. Chim. **91**, 148; **95**, 162.

Even if the cause of the acid nature was to be found in the chlorine, iodine, etc., rather than in the hydrogen, still the latter was the common constituent of them all, and hence better adapted to the formation of a name. Davy's investigations upon chloric and iodic acids lead him to much more general views. "Acidity does not depend upon any *peculiar* elementary substance, but upon *peculiar combinations* of various substances."[61]

At this time he seeks to prove that it is not oxygen which determines the peculiar character of an acid. Thus, for example, when oxygen is united to common salt, the neutrality of the substance is not disturbed; whereas, on the other hand, the saturating capacity of chloric acid is not altered when all the oxygen is removed from it. This obliges Davy no longer to regard chloric acid (in accordance with Lavoisier's view) as an oxide of the radical chlorine, which, combined with water, forms the hydrated acid. He finds that, without water, chloric acid cannot exist; and for this reason he regards it as a ternary compound of hydrogen, chlorine, and oxygen. Again, the existence of euchlorine, which he obtains from chloric acid and hydrochloric acid,[62] provides him with a reason against Lavoisier's hypothesis regarding acids.

The principles of a new theory of acids are included in Davy's discussions; but he did not follow them up sufficiently, otherwise they might have prevented the distinction which now began to be drawn between acids which did and those which did not contain oxygen. The same remark holds likewise with respect to Dulong, who had read a paper before the French Academy in 1815, in which he had stated his view regarding acids. This paper, unfortunately, does not appear to have been printed *in extenso*, and therefore I am able to give but little account of it.[63] Dulong on this occasion examined oxalic acid. The behaviour of some of its salts, which give off water when heated, led him to the opinion that the acid might be regarded as a hydrogen compound of carbonic acid—hydro-carbonic acid. On saturation with a metallic oxide, the oxygen of the oxide combines with the hydrogen of the oxalic acid to form water which can then be driven off, and a compound of carbonic acid with metal remains behind. Here we find the view for the first time represented (by Dulong and Davy) that the water produced during salt formation was not already contained in the (oxygenised) acid, and that, in a salt, it is not a metallic oxide but the metal, as such, that exists.

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[61] Phil. Trans. 1815, 219. [62] Ibid. 1811, 155; A.C.R. **9**, 63. [63] Mém. de l'Acad. 1813-1815, Histoire, p. cxcviii.; see also Schweigger's Journal, **17**, 229; Ann. Phil. **7**, 231.

It is stated that Dulong made a similar assumption for the other acids, but unfortunately the development of his ideas has not been handed down to us. Besides, hypotheses of this kind met with little approval at that time; voices were loud in their condemnation from the most different sides. Gay-Lussac declared himself emphatically against them;[64] and Berzelius (who was then beginning to exercise a predominant influence) seeing that he was obliged to admit the existence of acids free from oxygen, introduced a strict distinction between the latter and the acids containing oxygen, and so between the haloid and the amphid salts.

This single point in the system of Berzelius must not, however, be treated of separately, but the system must be dealt with as a whole. His views are of the utmost importance, since they dominated theoretical chemistry for twenty years. I shall devote the next lecture to their consideration.

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[64] Ann. Chim. [2] 1 (1816), 157.

LECTURE VI.

BERZELIUS AND HIS CHEMICAL SYSTEM—DULONG AND PETIT'S LAW —ISOMORPHISM—PROUT'S HYPOTHESIS—DUMAS' VAPOUR-DENSITY DETERMINATIONS—GMELIN AND HIS SCHOOL.

BERZELIUS adopts dualism as the basis of his system. Even before his time, the majority of compounds had been looked upon as consisting of two parts. A uniform mode of regarding them in this aspect became possible to a still greater degree in the light of the electro-chemical phenomena, and it is the great merit of Berzelius to have introduced this into the science and to have established it.

In his view, compound substances are produced by the arrangement of the atoms side by side.[1] Compounds of the first order are formed in this way from the smallest particles of the elements; these compounds give rise in turn to the formation of compounds of the second order; and so on. Berzelius, like his predecessors, seeks, in affinity, the reason for the combination of two atoms, but this again is for him, as it was for Davy, a consequence of the electrical properties of the smallest particles. He differs from Davy very essentially, however, in the manner in which he assumes the electrical distribution. But, quite apart from this, the two theories are not to be compared as regards their importance for our science. Davy, no doubt, advanced ingenious ideas as to the mode in which he considered the chemical and electrical phenomena to be inter-related; but from these hypotheses, by means of which a number of facts could be most excellently explained, he never succeeded in producing a theory which might serve as the foundation of a chemical system. Berzelius was the first to do this. He made it his life's task to establish in chemistry a uniform system which should be applicable to all the known facts; and he accomplished it. Hence his views are of far greater importance in the development of chemistry than those of Davy are.

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[1] Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'Electricité, 26. See also Berzelius, Lehrbuch der Chemie, First Edition, Vol. 3, part I. Compare also Schweigger's Journal. 6 (1812), 119.

According to Berzelius, it is not only when two substances are brought into contact that electricity is generated, but it is a property of matter; and in every atom, two oppositely electrical poles are assumed.[2] These poles do not, however, contain equal quantities of electricity. The atoms are unipolar, the electricity of the one pole predominating over that of the other; and thus every atom (and therefore every element) appears to be either positively or negatively electrical. In this respect it is possible to arrange the elementary substances into a series, so that each member is always more electro-negative than the next succeeding one. Oxygen stands at the top, and is absolutely electro-negative,[3] while the other substances are only relatively positive or negative according as they are compared with elements which come before them or after them in the electrical series. This series does not constitute a table of affinities in the Geoffroy-Bergman sense; and it does not express the affinity of the individual substances for oxygen, for example. Berzelius has not forgotten Berthollet's teaching, that affinity is not of a constant character and independent of the physical conditions, as he supposes this unipolarity to be; and he is also well aware that oxygen can be removed from metallic oxides by carbon or sulphur, that is to say, by other electro-negative substances. With him, affinity depends principally upon the intensity of the polarity, *i.e.*, upon the quantity of electricity which is contained in the two poles. This is variable, however, especially with changes of temperature.

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[2] Essai etc. 85. [3] In Schweigger's Journal, **6**, 129, where he states his electro-chemical theory in detail, Berzelius calls oxygen electro-positive.

Generally speaking, it is increased by supplying more heat, and this explains why certain combinations only take place at a high temperature.[4]

During the combination of two elements, the atoms arrange themselves with their opposite poles towards each other, and mutually discharge their free electricities, whereby the phenomena of heat and of light are produced. The old doctrine is explained at the same time—*Corpora non agunt nisi soluta* (substances do not interact unless dissolved), since free motion of the smallest particles is only possible in the liquid state. When a substance is subjected to the action of the electric current, the latter restores to the atoms their original polarity, whereby the substance breaks up into its constituents.

A compound of the first order is not electrically (nor yet chemically) inactive, since, during the combination, only one pole of each atom is neutralised ; it is still unipolar, and it can enter into further combinations (of the second order) which are likewise endowed with electrical forces ; but the intensities of these forces diminish, the higher the order of the compound becomes, since the stronger poles are, in general, neutralised first. According to Berzelius, the specific unipolarity of the oxides depends solely upon the radical or element combined with the oxygen. The latter gives rise to the most powerfully electro-positive and electro-negative substances (alkalies and acids) ; and as it cannot, therefore, be itself the cause in both cases, it cannot be the cause in either.[5]

All chemical reactions, and, consequently, the phenomena of heat and light that accompany them, are, according to Berzelius, produced by electricity, which "thus seems to be the first cause of the activity all around us in nature."[6]

If a substance C is to decompose the compound AB, so that B may become free, then C must be able to neutralise a greater amount of the electrical polarity of A than B can. Further, a mutual exchange between AB and CD only occurs if the electrical polarities are better equalised in AC and BD than they were previously. In reactions of this kind, Berzelius, like Berthollet, assumes an influence upon the resulting phenomena, of the quantities of the substances present and of cohesion; but he differs from Berthollet in regarding the affinity as a function of the electrical polarity, and as independent of the saturating capacity of the substance.

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[4] Lehrbuch. Second Edition, Vol. 3, Dresden (1827), part I, 73-74.

[5] Ibid. 76. [6] Ibid. 77.

This theory constitutes the basis of the dualistic theory of chemical composition. Berzelius establishes it as follows:—[7]

"If the electro-chemical views are accurate, it follows that every chemical combination depends wholly and solely upon two opposite forces, namely, the positive and the negative electricities, and that every compound must be composed of two parts, united by the effects of their electro-chemical reactions, since there is not any third force. From this it follows that every compound substance, whatever the number of its constituents may be, can be divided into two parts, of which the one is positively and the other is negatively electrical. Thus, for example, sulphate of soda is not composed of sulphur, oxygen, and sodium, but of sulphuric acid and soda, each of which can, in turn, be separately divided into an electro-positive and an electro-negative constituent. In the same way, also, alum cannot be regarded as immediately composed of its elementary constituents, but is to be looked upon as the product of the reaction of sulphate of alumina, as negative element, with sulphate of potash, as positive element; and thus the electro-chemical view justifies what I have said with respect to compound atoms of the first, second, third, etc., orders."

As may be perceived from this, Berzelius had formed a definite opinion as to the composition of compounds, and he went so far with this opinion, that he regarded as inadmissible the assumption, which lies readiest to hand, that the substance is composed of its elementary constituents. He thought he knew the arrangement of the atoms in compounds so minutely (principally from the decompositions which they underwent when subjected to the influence of the electric current), that he only regarded one particular view as possible.

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[7] Lehrbuch. 3, part I, 79-80.

As an appendix to the compounds, Berzelius takes solutions into consideration. He does not place these in the same class with the compounds, because a disappearance of heat is observed during their formation, and therefore no electrical discharge can take place in the operation.[8]

Before proceeding to the further statement of the system of Berzelius (especially before turning to his interesting and extremely important method of atomic weight determinations) I wish to say something about the nomenclature[9] and the system of notation,[10] which he had proposed some years before. In doing so, I can be all the more concise, as the former is merely the perfecting of the system introduced by Guyton, Lavoisier, Berthollet, and Fourcroy,[11] and both are, no doubt, well known. I can, therefore, confine myself to what is of essential importance, or is characteristic of the point of view of Berzelius.

Substances are divided into ponderables and imponderables. Amongst the latter we find electricity, magnetism, heat, and light. The former are divided into elements and compounds, solutions and mixtures. Amongst the simple substances, Berzelius places the metals and the metalloids. He uses a word here which Erman had employed before him for designating the metals of the alkalies and of the earths;[12] but Berzelius is the first to give it the meaning that we still attach to it.

The oxygen compounds are either called oxides or acids. The substances of this class which possess neither basic nor acid properties, and contain relatively little of the negative element, are called sub-oxides. The basic salt-forming oxygen compounds are designated oxides; when an element or a radical forms two substances of this kind, these are distinguished by the terminations of the specific name. This is very easy in the Latin nomenclature (which Berzelius proposes to employ); for example, oxidum ferrosum (with the smaller ratio of oxygen) and oxidum ferricum. Finally, superoxides are also distinguished. These contain a relatively large proportion of oxygen, and must be reduced before they form salts.

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[8] Lehrbuch. 3, part I, 80.

[9] Journ. de Phys. 73, 253.

[10] Essai etc, 111.

[11] Compare p. 32.

[12] Gilb. Ann. 42, 45.

What Berzelius says respecting compounds with water, is of interest. According to him, water may occur in compounds, combined in three different ways. It plays the part, either of an acid, as in the caustic alkalies, or of a base, when it unites with acids. In both of these cases it is called water of hydration, and is distinguished from water of crystallisation which unites with salts, and can be separated from these again, without their being, thereby, essentially changed in their nature.

The system of notation of Berzelius is original with himself, and, up to the present, it has always proved so thoroughly practical that we have retained his proposals almost without alteration. In his system, the atom of an element is represented by the initial letter of the Latin name of the element; and by placing the symbols side by side, the atoms of compounds are obtained. When several atoms of one element occur in a compound, a figure giving the number of these is placed after the letter, and above (or below) the line. The so-called double atoms (*i.e.*, two atoms of an element, which occur together) constitute an exception to this; in these the symbol for the atom is "barred."[13] Thus, for example, Ħ = H_2, or two atoms of hydrogen; ĦO = H_2O, or one atom of water, consisting of two atoms of hydrogen and one of oxygen, etc.

In the cases of more complicated compounds, several letters are separated from others by the sign +; and the mode of division is dependent on the dualistic view. For the sake of shortness, the atom of oxygen is often represented by a point, and that of sulphur by a vertical stroke; and in compounds, these marks are placed above the symbol of the element with which the oxygen or sulphur is combined—a method of writing formulæ that has now, however, been abandoned.

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[13] Lehrbuch. 3, part I, 108.

With these indications, we shall now leave this matter, and pass on to a much more important subject in the system of Berzelius, that is, to the mode by which he determined the number of atoms in a compound. He was the first who took account of purely chemical facts in these determinations. He rejects Dalton's rules entirely, pointing out, with justice, their groundlessness:—"When only one compound is known, there is surely something arbitrary in assuming that it consists of one atom of each element, altogether regardless of the other relations of the compound.[14]

Berzelius tries to establish the view, however, that regularities must exist, which determine the number of the atoms that mutually combine with one another.[15] He argues that if an unlimited number of atoms of one element could combine with an unlimited number of atoms of another, there would, in this way, be produced an infinite number of compounds which would differ so little in composition that even our best analyses would fail to show any difference. The view that substances consist of indivisible atoms, and that chemical compounds are produced by the arrangement of these atoms side by side, is not sufficient to explain multiple proportions. In the combination of atoms, special laws must prevail which limit the number of the compounds; and it is upon these laws, in particular, that chemical proportions depend.

He finds his first basis in Gay-Lussac's law of gaseous volumes.

This law appears to him to permit of an unequivocal decision of the question, since, with him, atom and volume are identical in the case of simple gases. "We know, for example, with certainty the relative number of atoms of nitrogen and of oxygen in the different stages of oxidation of nitrogen; that of nitrogen and of hydrogen in ammonia; that of chlorine and oxygen in the different stages of oxidation of chlorine;"[16] and so on. Amongst the gases, the law of multiple proportions finds confirmation in Gay-Lussac's rule ; and, by measuring the volumes, Berzelius can here determine the number of atoms which mutually combine with one another. For example, since two volumes of hydrogen unite with one volume of oxygen, water consists of two atoms of hydrogen and one atom of oxygen. He cannot conceive how anyone can be of a different opinion, and he engages in controversy with Thomson, who only assumes half as many atoms in one volume of hydrogen as in one volume of oxygen.

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[14] Lehrbuch. 3, part I, 88.

[15] Essai etc. 28.

[16] Lehrbuch. 3, part I, 89.

"It has been assumed that water is composed of an atom of oxygen and an atom of hydrogen ; but since it contains two volumes of the latter gas for one of the former, it was concluded that in hydrogen and in inflammable substances generally, the volume weighs only half as much as the atom, while in oxygen, volume and atom have the same weight. As this is only an arbitrary assumption, the accuracy of which cannot even be tested, it appears to me much simpler and more conformable with probability to assume the same relation of weight between the volume and the atom in the combustible substances as in oxygen ; because there is nothing which should make us suppose a difference between them. If water is regarded as composed of two atoms of radical and one atom of oxygen, then the corpuscular (atomic) and the volume theories coincide, so that their difference only consists in the state of aggregation in which they present the substances to us."[17]

It must be mentioned that Berzelius does not extend to the compound gases, his view as to the identity of volume and atom, but considers that the atoms of these neither occupy the same space as the atoms of the elements nor show uniformity of volume amongst themselves. That this is so, follows from his atomic weight estimations. With him, H = 1 = 1 volume or 1 atom of hydrogen ; $H_2O = 18 = 2$ volumes or 1 atom of water; ~~HCl~~ = 73 = 4 volumes or 1 atom of hydrochloric acid, etc.[18]

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[17] Lehrbuch. **3**, part I, 44-45. [18] It is true that he calls $HCl = 36.5$ an atom of hydrochloric acid and says ~~HCl~~ is the double atom (see Lehrbuch), but for the most part he actually employs the formula ~~HCl~~. I return to this again, however, further on.

Berzelius does not adopt the distinction between physical and chemical atoms, introduced by Avogadro and Ampère; and he endeavours to surmount the difficulty which had led Dalton to regard Gay-Lussac's law as inaccurate, by completely separating from one another the elementary and the compound gases.

It is clear that the law of gaseous volumes, together with the conclusions that Berzelius draws from it, is insufficient. It can only be used to determine the relative number of atoms in a very few compounds, and the founder of the first chemical system is, therefore, obliged to seek for other generalisations of more universal validity. He advances the following rules,[19] which are intended, however, to apply to inorganic compounds only.

I. One atom of an element combines with 1, 2, 3, etc., atoms of another element.

He does not state the limit. In 1819, he thinks that more than four atoms of one element seldom combine with one atom of another; afterwards (1828) he drops this limitation.

II. Two atoms of an element combine with 3 or with 5 atoms of another element.

This rule leads him to a discussion of the question as to whether a compound of 2 atoms of one element with 4 or with 6 of another element is identical or not with the combination of 1 atom of the first element with 2 or with 3 of the second. In his Text-book (1828) he leans to the latter opinion; by this time, isomeric compounds were known.

The laws of combination of compound atoms of the first, second, and third orders are quite similar, but certain limitations here come into play, arising from the fact that when compound atoms combine, they have either the electro-negative, or else, less frequently, the electro-positive constituent common to both, and the proportions in which these atoms then combine are determined by the common element in such a way that the quantities of the latter in the one constituent stand to those in the other as 1 to 1, 2, 3, 4, 5, 6, etc.; as 3 to 2 or 4; or finally, as 5 to 2, 3, 4, $4\frac{1}{2}$, and 6.[20]

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[19] Essai etc. 29-30.

It is interesting to see how, by the aid of these rules, Berzelius determines the number of atoms contained in a compound. As an example, I choose the oxygen compounds, which are unquestionably of the greatest importance.

Berzelius believes he has discovered (especially from the consideration of the proportions by volume in the case of gases) that it is usually the electro-negative constituent of which several atoms occur, and, therefore, in the case to be examined here, the above mentioned rules take the following form.[21]

> I. When an element or radical forms several oxides, and the quantities of oxygen in these, as compared with a given quantity of the other element, stand to each other as 1 to 2, it must be assumed that the first compound consists of 1 atom of radical and 1 atom of oxygen; the second, of 1 atom of radical and 2 atoms of oxygen (or 2 atoms of radical and 4 atoms of oxygen). When the proportions are as 2 to 3, the first compound consists of 1 atom of radical and 2 atoms of oxygen; the second, of 1 atom of radical and 3 atoms of oxygen, and so on.

In conformity with this rule, Berzelius, in 1819, writes soda NaO_2, and the peroxide NaO_3; and his formulæ for the other oxides are similar. Thus it comes about that the atomic weights which he proposes for the metals at this period, are double those which he definitely adopts afterwards (1828).[22] Influenced by reasons which we shall learn immediately, he makes, in his Text-book, the following addition to Rule I:—[23]

> When the proportion of the quantities of oxygen in two compounds is as 2 to 3, then in the first, 1 atom of radical can also be combined with 1 atom of oxygen, and, in the second, 2 atoms of radical can be combined with 3 atoms of oxygen.

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[20] Lehrbuch. 3, part I. 40.

[21] Essai etc. 118.

[22] Berzelius, Jahresbericht 1828, 73.

[23] Lehrbuch. 3, part I, 90.

II. When a positive oxide combines with a negative one (a base with an acid, for example), the oxygen in the latter is a multiple, by a whole number, of that in the former, and this number usually is, at the same time, the number of the oxygen atoms in the negative oxide.

These are the only two rules which Berzelius advances in 1819 in his theory of chemical proportions. In the translation of the second edition of his Text-book (the first German edition) new rules are added, called forth by Mitscherlich's discovery of isomorphism, and by the relations which Dulong and Petit had found (1819) between the atomic weights and the specific heats of solid elements.

Since both of these investigations are of the greatest importance with respect to the views of Berzelius upon the question now under discussion, I shall here introduce the results of these investigations, and shall then proceed with the consideration of the atomic weight determinations.

Dulong and Petit proved, by exact experiments,[24] that the products obtained by multiplying the specific heats of bismuth, lead, gold, platinum, tin, silver, zinc, tellurium, copper, nickel, iron, cobalt, and sulphur, by the respective atomic weights of these elements, are almost identical; and from this fact they drew the conclusion that the same regularity would hold with respect to all the elements and would lead to the exact determination of their atomic weights.

In order to establish the law, Dulong and Petit had assumed the atomic weights of most of the metals, with reference to that of sulphur, to be only half as great as Berzelius had stated them in 1819. They assumed 201 for the atomic weight of sulphur ($O = 100$), as Berzelius had done, and then made $Fe = 339$, whereas Berzelius had adopted 693. According to their law, the atomic weight of silver was only one-fourth of Berzelius' number. In the cases of tellurium and of cobalt, they arrive at results which are still further at variance with his, but these do not merit any confidence, as later observers (Regnault[25] and Kopp[26]) have found other numbers which agree better.

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[24] Ann. Chim. [2] **10**, 395.

I may take this opportunity to state that Neumann showed, in 1831,[27] that Dulong and Petit's law may also be extended to compounds of analogous composition; that is to say, the specific heats of these compounds multiplied by their equivalent weights (as Neumann calls them) give equal products. The law was proved, in particular, for the carbonates and the sulphates.

Before I pass on to Mitscherlich's interesting results, I wish to make some historical remarks by way of preface. With Hauy, the crystalline form (primitive form) was an important characteristic for the determination of the nature of a substance; difference of form being, in his view, a ground for assuming a different composition,[28] although Berthollet disputed this.[29] Gay-Lussac observed, in 1816, that crystals of potash alum increase in volume in a solution of ammonia alum, without altering in shape.[30] Beudant[31] also made very interesting statements in this connection; and, as early as 1817, J. N. v. Fuchs[32] drew attention to the similarity of the crystalline forms of arragonite, strontianite, and cerussite. Gehlen stated that he had succeeded in preparing crystals of alum with soda.[33]

These were isolated observations, which were insufficient to overthrow Hauy's doctrine, and which only attained to any importance through Mitscherlich's discovery of isomorphism.[34] In 1820, Mitscherlich established the fact that the corresponding phosphates and arseniates, with the same number of molecules of water, possess the same crystalline form, so that even the secondary forms coincide. Even at that time, the same number of atoms was assumed to be present in both acids, and thus Mitscherlich arrived at the idea that it was the similarity of atomic constitution which gave rise to the identity of form. And he really succeeded in confirming this opinion by a series of facts. He called those substances isomorphous, which exhibit the same crystalline form in corresponding compounds, and which, since they can crystallise together, replace one another in indefinite proportions. He pointed out the isomorphism of selenic acid and sulphuric acid ; that of magnesia, zinc oxide, nickelous oxide, ferrous oxide, etc., in their neutral sulphates, etc. ; that of alumina, ferric oxide, and manganic oxide. He also showed that Beudant's observation, in accordance with which iron vitriol and zinc vitriol (two salts of different crystalline form, and containing different proportions of water) crystallise together, depends upon the fact that the proportion of water in the one compound is changed, and becomes the same as that in the other.

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[25] Ann. Chim. [2] **73**, 5; ibid. [3] **1**, 129; **9**, 322 etc.
[26] Annalen, Supplementary Vol. **3**, 291.
[27] Pogg. Ann. **23**, 1.
[28] Traité de minéralogie.
[29] Stat. Chim. **1**, 433; E. **1**, 432.
[30] Kopp, Geschichte. **2**, 406.
[31] Ann. Chim. [2] **4**, 72; **7**, 399; **8**, 5; **14**, 326.
[32] Schweigger's Journal. **19**, 133.
[33] Ibid. **15**, 383, Note.
[34] Ann. Chim. [2] **14**, 172; **19**, 350; **24**, 264 and 355.

Other observers confirmed Mitscherlich's view by means of many observations,[35] so that, at that time, much stress was laid upon the crystalline form of substances; and chemists supposed that they possessed, in this character, an excellent means of obtaining information regarding their atomic constitution. It was Berzelius, in particular, who, instantly recognising the bearing of the great discovery, applied it to the extension of his system. Isomorphism led him to the following rule :—[36]

> III. When one substance is isomorphous with another in which the number of atoms is known, then the number of atoms in both is known, because isomorphism is a mechanical consequence of similarity of atomic construction.

Guided by these rules, Berzelius endeavours to determine the number of atoms contained in a compound, and from this, he can then deduce the atomic weights. He is quite conscious that his rules, in many cases, cannot lead him to a decisive determination, and that it is really in the cases of gaseous elements only that they can give unequivocal results. But just because he knows upon what shaky grounds he is proceeding, he acts with the greatest caution; and it is marvellous how often, guided by an acute judgment, he hits upon the correct number, where almost every criterion is wanting.

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[35] Literature in the article "Isomorphismus" in the Handwörterbuch der Chemie, edited by Liebig, Poggendorff, and Wöhler. In the article "Isomorphie" in the second edition of this Dictionary, Arzruni enters particularly into the subsequent development of the doctrine of isomorphism.

[36] Lehrbuch, 3, part I, 91.

In the case of the oxides, Berzelius constructs for himself a series which furnishes him with the relative quantities of oxygen with which certain weights of the metals combine. In doing so, he does not require to construct a series of this kind for every metal. By calling Mitscherlich's law to his assistance, he is able to supply the places of any stages of oxidation that are wanting in the case of a given element, by those of an isomorphous element. The series is :—[37]

	Relative Proportion of Oxygen.
Cuprous oxide - - - - - -	1
Cupric oxide, ferrous oxide, etc. - -	2
Ferric oxide, manganic oxide, minium -	3
Lead peroxide, manganese peroxide - -	4
Manganic acid - - - - - -	5

I also give, below, a similar but more accurate tabulation, from the year 1835.[38]

Cuprous oxide - - - - - -	1
Cupric oxide, ferrous oxide, etc. - -	2
Ferric oxide, manganic oxide, etc. - -	3
Lead peroxide, manganese peroxide, etc. -	4
Nitric acid, chloric acid, etc. - - -	5
Perchloric acid, permanganic acid, etc. -	7

In the compounds noted here, Berzelius assumes 1, 2, 3, 4, 5 (and 7) atoms of oxygen; thus making the simplest assumption possible. It is then only a matter of determining, in addition, the number of atoms of the radical or element that is united with the oxygen. His series does not furnish any information about this, and therefore he seeks for other generalisations. He now rejects the apparently most natural assumption of 1 atom of radical, which he had made in 1819, since it leads him to atomic weights that are not in harmony with Dulong and Petit's law. He finds a new starting-point (except for silver, tellurium, and cobalt) by assuming the presence in compounds of two atoms of the element concerned, and thus he obtains the following series for the stages of oxidation of the most of the metals :—

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[37] Lehrbuch. 3, part I, 97.

[38] Lehrbuch. Third Edition, 5, 89.

$$R_2O,\ RO,\ R_2O_3,\ RO_2,\ R_2O_5,\ (R_2O_7),$$
$$\text{or } \cancel{R}O,\ RO,\ \cancel{R}O_3,\ RO_2,\ \cancel{R}O_5,\ (\cancel{R}O_7),$$

where he writes $\cancel{R}O$ instead of R_2O_2, and $\cancel{R}O_2$ instead of R_2O_4.

Berzelius advances several grounds which appear to tell in favour of the accuracy of his choice. The most commonly occurring oxides, such as cupric oxide, magnesia, lime, etc., receive the simplest formula, RO ; further, the oxygen compounds of nitrogen and of chlorine, in which he knows, from the volumes, the number of atoms, can be made to fit in with his arrangement. On this account, he regards this series as one that occurs generally distributed, calls it the nitrogen series, and contrasts the sulphur series with it.

Berzelius finds the relative quantities of oxygen that combine with sulphur to be 1, 2, $2\frac{1}{2}$, and 3. Hence, he writes the stages of oxidation of this element : SO, SO_2, S_2O_5, and SO_3. He endeavours to arrange all the oxygen compounds, as far as possible, in the sulphur and nitrogen series, and assumes, for example, SiO_3 as the formula for silicic acid, corresponding with sulphuric acid, an assumption which afterwards gave occasion for many discussions.

The sulphur compounds (sulphides) are regarded as constituted in a manner analogous to the oxygen compounds. He writes sulphuretted hydrogen $\cancel{H}S$, because water is $\cancel{H}O$.

In calculating the atomic weights which he deduces from these considerations, Berzelius starts from $O = 100$, but, in order to permit of comparison with earlier and with subsequent statements, and since it is merely a question of the relative magnitudes of the numbers, I shall give his values, calculated with reference to oxygen as standard with atomic weight = 16.[39]

Element and Symbol.		Atomic Weight (O = 16) (Berzelius).	Atomic Weight (O = 16) (International Commission, 1905).
Arsenic	As	75.33	75.0
Calcium	Ca	41.03	40.1
Carbon	C	12.25	12.0
Chlorine	Cl	35.47	35.45
Iodine	I	123.20	126.97
Iron	Fe	54.36	55.9
Manganese	Mn	57.02	55.0
Mercury	Hg	202.86	200.0
Nitrogen	N	14.18	14.04
Oxygen	O	16.00	16.00
Phosphorus	P	31.43	31.0
Silicon	Si	44.47	28.4
Silver	Ag	216.61	107.93
Sodium	Na	46.62	23.05
Sulphur	S	32.24	32.06

Before I conclude the consideration of Berzelius' system, I shall add a few words with respect to the formulæ of hydrochloric acid and of ammonia. The atoms of these substances are represented by HCl and NH_3,[40] showing that Berzelius did not identify the conceptions of atom and equivalent in all cases, although he employs the names indiscriminately. This might, of course, be regarded as no real exception, since, generally speaking, the double atoms ~~HCl~~ and ~~NH~~$_3$ are alone employed. Naturally, it is difficult to give an exact account of the views of one who is no longer alive; but it is in every case necessary to take the different periods into account. I believe then that Berzelius, at first, and till about 1830, tried to extend the law of volumes as far as possible (even to compounds as compared with one another), and that this was a reason for assuming the formulæ HCl and NH_3 for hydrochloric acid and ammonia; but that afterwards, influenced especially by Dumas' investigations,[41] he placed much less reliance upon this law, and applied it to the permanent (and elementary) gases alone.[42] He was then no longer prevented from believing in an agreement between equivalent and atom, even in these substances, and he employed only the formulæ ~~HCl~~ and ~~NH~~$_3$.

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[39] Berzelius, Jahresbericht 1828, 73; the values are also to be found there calculated for H = 1. [40] Lehrbuch. Third Edition, 2, 187 and 344.

It follows, from the foregoing, that Berzelius did not admit the distinction between the physical and the chemical atom, and he thereby establishes an essential difference between elements and compounds. According to him, the atoms of the elementary gases occupy, in general, one half (or one quarter) the space occupied by the atoms of the compound gases. Whilst similarity in behaviour with respect to changes of pressure and of temperature was a sufficient reason for assuming the same number of atoms in equal volumes of hydrogen and of oxygen, the same reason was insufficient to justify the same conclusion with regard to chlorine and hydrochloric acid. There was an inconsequence in this, but it was of no material importance, since the experiments bearing most closely upon the matter appeared to negative any general applicability to it of the law of gaseous volumes.

The chemical edifice which Berzelius erected was a wonderful one, as it stood completed (for inorganic substances) at the end of the third decade of the nineteenth century. Even if it cannot be said that the fundamental ideas of the system proceeded exclusively from himself, and if he was indebted to Lavoisier, Dalton, Davy, and Gay-Lussac for a great deal, still it was he who moulded these ideas and theories into a connected whole, adding also much that was original. His electro-chemical hypothesis no doubt had points of similarity with that of Davy, but, in spite of that, it was essentially different from it. Besides, the first method of atomic weight determination, of moderately general applicability, proceeded from Berzelius; and this method was so extraordinarily serviceable that it rendered possible the fixing of these most important numbers, so that alteration was necessary in only a few cases.

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[41] Ann. Chim. [2] 49, 210; 50, 170.

[42] Lehrbuch. Third Edition, 5, 82.

It will thus be understood how the system of Berzelius became the prevailing one, and why his judgment was authoritative. The publication of his yearly reports (*Jahresberichte*), which began to appear in 1821 and were employed not merely for reporting but also for criticising, contributed to increase his influence. Hence the ideas of others possess only a subordinate interest, but still I wish to state the views of some of his contemporaries, so that I may the better characterise the period under review.

British chemists had not yet come to a decision with respect to Dalton's conception of the atom and Wollaston's of the equivalent. Very little of much importance had meanwhile been accomplished in Great Britain. The only thing to which I wish to refer is the hypothesis of Prout, which was the occasion of much discussion.

Prout, in 1815, thought it was possible to show that the atomic weights of the gaseous elements are multiples, by whole numbers, of that of hydrogen.[43] Stated in this way, the matter seems to be of small importance; but it gains interest from the fact that, if it is admitted to be generally applicable, it almost necessarily leads to the assumption of a primordial form of matter, and to the view that the manifold peculiarities of substances are explicable by the varying distribution of this matter in space. Thomson[44] set himself the task of extending the statement of Prout to all the elements, and, for this purpose, he carried out a large number of atomic weight determinations. His results are worthless, however, as Berzelius somewhat bluntly points out to him.[45]

At a later period, Prout's hypothesis was taken up again by Dumas,[46] after it had been shown that a more accurate determination of the numbers told in its favour. In particular, the atomic weights of the best known elements, such as oxygen, hydrogen, nitrogen, carbon (chlorine?), bromine, iodine, etc., appeared to be in harmony with it. Stas has proved, however, by means of experiments in which the highest degree of accuracy and completeness was attained,[47] that even in the case of those elements which appeared in accord with it, the hypothesis does not in any instance hold rigidly, and can only be looked upon as an approximation.

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[43] Ann. Phil. **6**, 321. [44] Thomson, An Attempt to establish the First Principles of Chemistry by Experiment, 2 vols. London (1825). [45] Berzelius, Jahresbericht 1823, 40. [46] Ann. Chim. [3] **55**, 129.

The highly important theory established by Newlands, Lothar Meyer, and, especially, Mendelejeff, dealing with the periodic relation of the properties of the elements to the magnitudes of their atomic weights, can only be entered upon in a subsequent lecture.

In France, the law of volumes in its most extended sense became the basis of the atomic considerations. It was Dumas, especially, who took up a very decided position in this connection. He shows that the conception of the equivalent cannot be employed as the basis of a system, because it loses its significance when it is extended further than to acids, to bases, and to other substances which closely resemble each other (oxides and sulphides); and, especially, that it becomes quite vague when the attempt is made to identify the equivalent with the combining weight,[48] since very many substances can combine in several proportions. Thus, for example, 8 parts of copper are combined with 1 part of oxygen in cuprous oxide, while for 8 parts of copper, 2 parts of oxygen are contained in cupric oxide. Calculated from these numbers, the equivalent (combining weight) of copper, referred to that of oxygen as unity, is 8 or 4.

Dumas believes that, by adopting Avogadro's hypothesis as a basis, he has obtained a sure guide in considerations regarding atomic weights. He assumes that in equal volumes of all gases (at the same temperature and pressure) there is the same number of (physical) atoms, but that these are still divisible by chemical means. "We call *atoms*, the groups of chemical molecules that exist isolated in the gases. The atoms of the elementary gases always contain a certain number of molecules which is unknown to us."[49] The ratio of the densities of the gases gives Dumas the ratio of their atomic weights. In fixing the atomic weights of the solid elements he makes use of the law of Dulong and Petit, which he regards, accordingly, as holding for groups of chemically smallest particles—molecules, as we should now say. Further, he employs for the same purpose the relative densities of volatile compounds, making assumptions, from analogy, as to the volume relations of the unknown elementary gases contained in them. Thus he finds the atomic weight of sulphur from the density of sulphuretted hydrogen, which he assumes to be constituted like water and to consist of 2 volumes of hydrogen and 1 of sulphur vapour; and that of phosphorus from phosphuretted hydrogen, which he supposes to be constituted like ammonia. His determination of the atomic weight of carbon is noteworthy. He deduces it from the relative densities of ethylene and of marsh gas. He assumes in the latter (as Gay-Lussac had also done previously) 2 volumes of hydrogen for 1 of carbon vapour, and in the former, equal volumes of the two. He thus finds the atomic weight of carbon to be one half of what Berzelius had estimated it to be, that is 6, if that of hydrogen is assumed equal to 1. In general, however, the values which he assigns to the atomic weights of the better known elements are the same as those of Berzelius. Mercury, silicon, etc., form exceptions. Dumas does not state the weights of the chemically smallest particles.

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[47] Recherches sur les lois des proportions chimiques etc., Bruxelles 1865, and Recherches sur les rapports réciproques des poids atomiques, 1860.

[48] Dumas, Traité de Chimie appliquée aux arts. Paris (1828-46).

Berzelius contested the principles of the system just considered, although they were so closely related to his own.[50] He thinks that it is absurd to assume fractions of atoms, and says it was formerly the custom to abandon hypotheses as soon as they led to absurdity. Dumas stands entirely isolated in his views, but, in spite of this, he would probably have adhered to them, had he not himself discovered facts which caused him to doubt the accuracy of Avogadro's hypothesis.

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[49] Dumas, Traité. 1, 41.

[50] Berzelius, Jahresbericht 1828, 80.

Dumas was not only an ingenious thinker, but he was also an excellent experimenter; and, since he had chosen the densities of gases and vapours as the basis of his atomic theory, he thought it necessary to increase our knowledge respecting these densities. He succeeds in elaborating a method for carrying out determinations of this kind at high temperatures, and employs it for ascertaining the relative densities of the vapours of iodine, phosphorus, sulphur, mercury, etc.[51] His results, from which he anticipated confirmation of his views, lead him to abandon them. He finds the density of phosphorus vapour to be twice as great, and that of sulphur vapour to be three times as great as he had previously assumed, whilst that of mercury vapour is only one half of what he had supposed. In view of these facts he begins to doubt; in fact he declares that even the simple gases do not contain, in the same volume, the same number of chemical atoms. According to him, the assumption may still be made that there is the same number of molecular or atomic groups present in equal volumes of all gases; but that this is only a hypothesis, which cannot be of any service.[52] Dumas is obliged to admit that Gay-Lussac's law, when applied in the way he had applied it to the determination of atomic weights, furnishes erroneous results. Hence he believes that it cannot be employed for this purpose, and he now abandons Avogadro's hypothesis.

Berzelius, too, can no longer maintain the identity of volume and atom in the cases of the elementary gases, and has to confine his proposition to the incondensable elastic fluids.[53] It must be admitted that the law, when so stated, was not capable of any extended application, and was more than insufficient for the determination of the atomic weights of the majority of the elements. And how did it fare with the other generalisations upon which his system rested? The hypothesis of Dulong and Petit was not without exceptions in its applicability, as I have already stated. The numbers deduced from it for silver, cobalt, and tellurium were not in harmony with Berzelius' determinations, that is, with the atomic weights required by the chemical analogies, and by isomorphism; so that even this hypothesis was not tenable when rigidly considered. Mitscherlich's law still remained, and the majority of chemists believed that it permitted of an unerring conclusion as to the atomic constitution. Other voices were heard, however, which indicated doubts, especially after Mitscherlich had shown that there are dimorphous substances, *i.e.*, substances which can occur in two crystalline forms.[54] Attention was drawn to the fact that, as the occurrence of dimorphism proved, the crystalline form of a substance was not determined solely by the number of its atoms.[55]

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[51] Ann. Chim. [2] **33**, 337; **44**, 288; **49**, 210; **50**, 170.

[52] Leçons. 268 and 270.

[53] See p. 92.

Of all the physical laws that had been applied to the determination of atomic weights, there thus remained not one upon which full reliance was placed. The conception of the atom was looked upon, in consequence, as uncertain and hypothetical. Chemists believed they would have to be contented with the combining weight or the equivalent, the latter of which had gained new support from Faraday's electrolytic law.[56] At the end of the fourth decade of the nineteenth century, we thus find the atomic theory—the most brilliant theoretical achievement of chemistry—abandoned and discredited by the majority of chemists, as a generalisation of too hypothetical a character. A new school had arisen, which had adopted Wollaston's equivalents, and which sought, successfully, to supplant the system of Berzelius.

At the head of this movement there stands L. Gmelin. The views of this chemist are of all the more importance from the fact that he expounded them in his excellent Hand-book;

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[54] Ann. Chim. [2] **24**, 264. [55] Ibid. [2] **50**, 171. [56] Experimental Researches in Electricity, Series **3**, § 377, Series **7** § 783 *et seq.* 1833-34.

which latter, on account of its completeness, had, at that time, already become widely distributed.

With Gmelin, there is no strict distinction between mixtures and compounds, and this proves that he does not believe in the real existence of atoms. Two substances, especially when they possess only a weak affinity for each other, can combine, according to him, in an infinite number of proportions; but the greater the affinity, the greater is their tendency to combine in few proportions only.[57] These proportions then stand to each other in simple relations. "There can therefore be assigned to every substance a certain weight in which it combines with definite weights of other elements. This weight is the stöchiometric number, the chemical equivalent, the mixture-weight or atomic weight, and so on. Compounds are composed in such proportions that one mixture-weight of one substance is united to $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, 4, 5, 6, 7, or more mixture-weights of the other." According to Gmelin, Gay-Lussac's law runs:—One measure of an elastic fluid substance combines with 1, $1\frac{1}{3}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 measures of the other.

His table of equivalents is well known. It ran:—$H=1$, $O=8$, $S=16$, $C=6$, etc. Water was written HO, and in formulæ generally, the endeavour was made to replace by simplicity what they had lost in conception and in purpose. Chemistry was to become a science confined to observation—indeed almost to description alone. Skill in manipulation was all that was required; speculation was banished as dangerous.

It had come to this then:—Inorganic chemistry, in connection with physics, had not been able to maintain the conception of the atom. It is my business to show, in the next lectures, how it was reintroduced into the science by means of organic chemistry.

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[57] Handbuch der theoretischen Chemie. Second Edition, 1821.

LECTURE VII.

ORGANIC CHEMISTRY AT THE COMMENCEMENT OF ITS DEVELOPMENT—ATTEMPTS TO DETERMINE THE ELEMENTARY CONSTITUENTS OF ORGANIC COMPOUNDS—ISOMERISM AND POLYMERISM—VIEWS REGARDING CONSTITUTION—RADICAL THEORY.

IN this lecture I shall endeavour to give an account of the development of organic chemistry. I have intentionally postponed this subject until now because I wished to consider it in a connected manner, because it had almost no influence during the first three decades of the nineteenth century upon the perfecting of general theories, and also because the views which constitute the basis of inorganic chemistry did not, at first, seem to be capable of any application to the organic branch of the science. Thus we find Berzelius, in 1828, treating the subject of the organic compounds separately. The electro-chemical theory, the law of multiple proportions, and the law of volumes did not appear to dominate substances derived from the animal and vegetable kingdoms; these substances were subject to the so-called vital force, the nature of which was wholly unknown and obscure. It only became possible to extend to organic chemistry also, the laws which held for inorganic substances, after the study of this part of the subject had further attracted thinkers to itself. The opinions and hypotheses to which the examination of the better known substances had led, had now to be turned to account in the younger branch of the science. It was dualism, in particular, which was now introduced into organic chemistry also.

Lavoisier had already assumed, as has been stated previously, that the acids consist of oxygen and a basis; and that, in inorganic compounds, the latter is an element, while in organic compounds it is a compound radical. The latter name had not been lost. The chemical nomenclature had been based upon it, and the dualism of Berzelius was a happy extension of it. All observations seemed to be in agreement with it. Thus the salts (at that time the best known class of substances) are formed from acid and base, and they can be decomposed again into these constituents. Why should we not endeavour to look upon organic compounds also as formed in a similar way? Since organic compounds (according to the view held at that period) consisted of at least three elements, any simple decomposition must still leave one part of a composite nature. Organic chemistry thus became the Chemistry of the Compound Radicals. In thus employing the term radical, its original definition was retained. After the removal of the oxygen from a substance, the residue which remained, and which, moreover, played the part of an element, was called a radical. Wöhler and Liebig remodelled this conception. In their admirable research on bitter almond oil and the allied compounds, they showed that we may assume the existence, in these substances, of an oxygenated group which remains unchanged in the majority of the reactions, and therefore behaves like an elementary substance. On this account, they called it the radical of bitter almond oil.

By this departure the first great step had been taken; organic chemistry had become independent; it had freed itself from the fetters which had been placed upon it; if, from within its own limits, it had not produced a new idea, it had at least given new and increased importance to one which was already held. From this time forward, it proceeds on its own way, and pays no heed to the limitations which some desired to place upon it. The very harmonious edifice of chemistry suffers in consequence. Every endeavour is made to adapt it to the new ideas. But it is in vain—the breach is unavoidable. The young science, quite conscious of its own strength, dares to make an assault upon the foundations, and, in spite of stays and props, the structure begins to totter. The attack upon the electro-chemical theory led to an embittered controversy between its supporters, with Berzelius at their head, and the adherents of the substitution theory or the theory of types. This controversy was triumphantly passed through by the latter, and led to the complete separation of organic and inorganic chemistry. At any rate the endeavour was still made to retain in the latter, as before, the dependence of the chemical upon the electrical forces, whilst the newest facts in the domain of organic chemistry appeared to be incompatible with this. Our science thus fell anew into two schools, and the principles which guided the one school were rejected by the other.

Simultaneously with the abandonment of the electrochemical hypothesis, the radical theory was also given up; there was now no longer any actual need for it, and, in the form in which it had been advanced, it was insufficient. A great deal had been discarded as useless, and therefore it is by no means inadvisable to inquire into the principles which still remained with the representatives of the new school. The views as to the preservation of the type, and as to substitution, although, of course, most valuable for the comprehension of many reactions, could scarcely be employed as the basis of a complete system. But amongst the ruins left upon the battlefield, and found there when it was cleared up, there was a jewel, which, although little heeded during the controversy, was now capable of becoming of great significance when the question was no longer one of getting rid of old views, but one of setting up new views in their stead. The atomic theory, despised by many, forgotten by some, was now destined to arise again in its original brilliancy, although a hard struggle was necessary. New foundations for the determination of the relative masses of the atoms had to be obtained. It was Gerhardt, in particular, who insisted on the necessity of fixing upon comparable quantities for these determinations. But whence was the standard to be derived? Liebig's polybasic acids, and Dumas' substitution, had at length taught chemists the difference between atom and equivalent, so that there could no longer be any question with respect to the latter. Recourse was again taken to Avogadro's hypothesis; but this still proved insufficient, and chemical reasons were required in order to convince chemists. Gerhardt, who received very substantial support from Laurent, exerted himself in vain to adduce decisive proofs of the accuracy of his ideas. At this juncture, Williamson's investigations appeared, and they gave a real foundation to the thoughts that had flitted before Gerhardt's mind. This gifted chemist had shown the way; and, in imitation of him, it was extensively followed, since it permitted of a direct comparison of the quantities entering into reaction. Thus there arose the conception of the chemical molecule. In Gerhardt's system, which was now rapidly gaining recognition, this conception found its formal expression in the theory of types.

I shall here conclude this sketch, in which I have indicated, in general outline, the different phases of the historical development; and I shall now proceed to a detailed account.

As early as the second half of the seventeenth century, Lemery separated organic from inorganic chemistry. He divided substances, according to their origin, into three classes, viz., mineral, animal, and vegetable.[1] The phlogistians occupied themselves chiefly with the first class. Scheele deserves to be mentioned as the discoverer of an extensive series of organic substances.[2] Lavoisier believed that compounds belonging to this class consisted of carbon, hydrogen, and oxygen; Berthollet proved the presence of nitrogen in substances of animal origin;[3] at a later date, it was recognised that all the elements can enter into organic combinations, but that carbon must never be absent.[4]

It is difficult to say what substances were regarded as organic compounds at the beginning of the nineteenth century. This class naturally included all substances occurring in the plant or animal organism, but from these there were prepared a large number of other compounds, whose position in the system had also to be determined; and a decision as to the class in which they were to be enumerated was often an arbitrary matter. Simplicity of composition was frequently a reason for placing substances in the inorganic class. With regard to many substances, the views as to their nature had changed in course of time; for example, in the case of the cyanogen compounds, which were first classed as organic and afterwards as inorganic substances. Wherever it was possible, Lavoisier's idea was upheld that in organic substances, the basis combined with oxygen, or the radical, consists of several elements. This gave rise, at a later date, to Liebig's definition of organic chemistry as the chemistry of the compound radicals.

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[1] Kopp, Geschichte. **4**, 241. [2] See pp. 10-11. [3] Journ. de Phys. **28**, 272. [4] Gmelin, Handbuch der Chemie. Fourth Edition, **4**, 3; **E. 7**, 4.

The study of the compounds belonging to this class lagged considerably behind that of the others. The reason lay partly in the easy alterability of these substances, and, thus, in the greater difficulty which their isolation presented; partly also in the scarcity of methods for their analysis. At the beginning of the nineteenth century, when qualitative analysis had already attained a high degree of accuracy, and even the quantitative method had found excellent exponents in Proust, Klaproth, and Vauquelin, Lavoisier's experiments with alcohol, oil, and wax, were the only ones in existence, designed to ascertain the composition of organic compounds; and these, as may be easily understood, were not very accurate.

It is thus explicable that Berzelius should still doubt, in 1819, whether the law of multiple proportions held in organic chemistry also.[5] He was well aware that when organic compounds unite with inorganic ones—organic acids with metallic oxides, for example—the same regularities are observed as in inorganic chemistry; but he believed the proportions in which carbon, hydrogen, oxygen, and nitrogen unite, to be so varied that Dalton's law lost its significance, simply because 1, 2, . . n atoms of one element could unite with 1, 2, . . m atoms of another. Nevertheless Berzelius himself afterwards assisted more than anyone else in extending the laws of stöchiometry to organic chemistry, inasmuch as he materially improved the method of elementary analysis employed at that time, and thereby provided himself and others with the means of ascertaining the composition of organic substances.

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[5] Essai etc., 96; compare also Lehrbuch. 3, part I, 151.

It may not be out of place to give some account here of the history of elementary analysis, just because the views respecting organic compounds were essentially changed in consequence of its development.

I shall not again revert to Lavoisier's method, which I have already indicated in an earlier lecture.[6] There are almost thirty years between his experiments and those of his nearest successors. I pass over the experiments of Saussure,[7] Berthollet,[8] etc., as well as the first labours of Berzelius[9] upon this subject. These furnished analytical processes that were sufficient, perhaps, in special cases, but cannot by any means be regarded as general methods. On the other hand, the investigation of Gay-Lussac and Thenard, in 1811, deserves our attention.[10] They burned the organic substance with potassium chlorate, by forming small pellets of the mixture and allowing these to fall into a perpendicularly placed tube, the lower end of which was heated red-hot. The tube was closed above by means of a stop-cock furnished with a recess designed for the reception of the pellets. The gases from the combustion had to make their escape through a side tube into a eudiometer, and they were there measured. Gay-Lussac and Thenard then absorbed the carbonic anhydride formed, and determined the oxygen left behind. They knew, further, the quantity of substance burned and the quantity of potassium chlorate mixed with it. By the help of Lavoisier's equation :—

Substance + Oxygen employed = Carbonic anhydride + Water they were then able to calculate the quantity of water produced by the combustion, and, therefore, the composition of the compound.

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[6] See pp. 28-29. [7] Journ. de Phys. **64**, 316; Bibliothèque britannique. **54**, No. 4; **56**, 344; Ann. Phil. **4**, 34. [8] Mém. d'Arcueil. **3**, 64; Mém. de l'Acad. 1810, 121. [9] Gilb. Ann. **40** (1812), 246. [10] Rech. phys. chim. **2**, 265.

Gay-Lussac and Thenard carried out the analysis of twenty substances in this way. Their results are moderately accurate, but the method still left much to be desired. The combustion was very violent; it was accompanied by explosion, and was, therefore, frequently incomplete.

The next great step in the development of elementary analysis was made by Berzelius in 1814.[11] By carrying out the combustion with a mixture of potassium chlorate and sodium chloride, he secured the much more moderate progress of the analysis. His method, also, differs very essentially and advantageously from the earlier one, in so far that he did not gradually introduce the substance intended for combustion into a red-hot tube, but instead, put the whole quantity of the substance, along with the oxidising material, into a tube which he gradually heated to redness in a horizontal position. Further, he was the first to weigh the water directly, which he did after having absorbed it by means of calcium chloride; whereas he determined the carbonic anhydride either by volume or by weight.

This mode of carrying out the analysis already approximates closely to the present method; it was still further improved by employing cupric oxide instead of potassium chlorate. This was first used by Gay-Lussac for nitrogenous substances,[12] but a year afterwards it was employed by Döbereiner in the combustion of substances free from nitrogen.[13]

Analyses were carried out by this process for more than ten years, until the method was modified by Liebig[14] in 1830, and brought into the form now employed. As a consequence of Liebig's investigations, elementary analysis became an easily accomplished operation, which, in so far as accuracy was concerned, might be placed alongside of other analyses. A rapid advancement of organic chemistry dates from this period. Since a simple and sure means of determining the composition of the substances was now available, investigations which had not previously been attempted on account of the endless difficulties associated with them, now became possible and were actually carried out.

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[11] Ann. Phil. **4**, 330 and 401. [12] Ann. Chim. **95**, 154; Ann. Phil. **7**, 357. [13] Schweigger's Journal. **17**, 369; compare also Chevreul, Recherches chimiques sur les corps gras d'origine animale (1823). [14] Pogg. Ann. **21**, 1; more fully in his "Anleitung zur Analyse organischer Körper." Braunschweig (1837); English Translation, by Gregory: "Instructions for the Chemical Analysis of Organic Bodies," Glasgow (1839).

No doubt many analyses had already been carried out by the method of Berzelius, and the conviction became more and more settled that the law of multiple proportions was applicable to organic compounds also, and that formulæ similar to those assigned to mineral substances could be assigned to them. But an important distinction was still drawn, in the third decade of last century, between these two classes of substances. It was supposed that the latter alone were producible artificially; while the synthesis of the former was wholly beyond our power and was reserved for the living organism, in which it was performed under the influence of the Vital Force. From such naturally occurring substances chemists had, it is true, learned to prepare, by dry distillation, by treatment with nitric acid, with alkalies, etc., other substances which were likewise classed amongst organic compounds, but these were, for the most part, simpler in composition, and the material existing in nature always remained the starting-point. In this connection, an excellent investigation for that period, by Chevreul, deserves to be mentioned,[15] in which the author showed that the fats consist of an acid and of glycerine (a substance discovered by Scheele), and that they should, accordingly, be placed in the series of ethers, where all those substances were classed which could be separated by means of alkalies into an acid and an indifferent substance (an alcohol).

This and similar investigations could not, however, shake the belief in a vital force under whose influence all organic compounds originated. As yet no one had succeeded in artificially preparing any substance occurring in the organism; but even this great step had not to be waited for much longer. For this discovery we are indebted to Wöhler, and with it he opened his long and brilliant scientific career.

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[15] Rech. Chim.

Wöhler had discovered cyanic acid in 1822,[16] and was occupied in its investigation when he made the observation, in 1828, that urea, a known product of animal life, was formed upon the evaporation of a solution of its ammonium salt.[17] It is true that the problem was not completely solved by this discovery. The synthesis from the elements was not yet possible, but still the most essential thing had been accomplished. From inorganic compounds (amongst which many at that time classed cyanic acid)[18] a substance had been prepared which had hitherto been found in the animal organism only. In spite of this, the revolution of ideas proceeded but slowly; it was still believed that the vital force could not be dispensed with, and some decades afterwards, scientific discussions took place as to its existence. Nowadays, when the materialistic tendency becomes more and more ascendant, there are few to be found who ascribe the production of organic substances to forces different from those that govern the production of mineral substances. It is true that the experimental science has made great progress in this respect also, since it has succeeded in preparing from their elements many organic substances. Thus Kolbe effected the complete synthesis of trichloracetic acid,[19] and Berthelot the syntheses of formic acid and of alcohol. The latter chemist inaugurated, with these researches, his brilliant series of synthetical investigations.[20]

It may appear remarkable to many persons, into whose hands a treatise on organic compounds published in the third decade of last century, or earlier, may chance to fall, that even at that time, when this department of chemistry was in so backward a state of development, experiments were made in order to obtain some information as to the constitution, or mode of arrangement of the atoms, of compounds. A pursuit of this kind may be regarded as idle speculation, and yet scientific chemistry was directed, at an early period, towards such considerations. This was owing to the phenomena of isomerism, into which, therefore, I must here enter with some detail.

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[16] Gilb. Ann. **71**, 95. [17] Pogg. Ann. **12**, 253; Quart. Journ. Science. 1828, **1**, 491. [18] Compare, for example, Dumas, Traité. **1**, 409. [19] Annalen. **54**, 145. [20] Berthelot, Chimie organique fondée sur la Synthèse, Paris (1860); see also his more recent investigations, Bull. Soc. Chim. [2] **7**, **113**, **124**, **217**, **274**, **303**, **310**, etc.

After chemists had begun to pay attention to the quantitative composition of substances, and especially after they had learned to regard constant proportions by weight of their constituents as a real characteristic of chemical compounds, it was assumed as a matter of course that the same composition per cent. always postulated the same properties. It was, of course, known that very many, and indeed most, substances occurred in several states: solid, liquid, and gaseous; crystalline and amorphous, etc.; but the sensation that the discovery of dimorphism made, shows us how great the tendency was at that time to regard physical and chemical properties as functions of the composition per cent. (and of the temperature). It must naturally have created much surprise to see that sulphur can appear in two crystalline forms; to hear that arragonite is pure calcium carbonate, and is therefore dimorphous with calc-spar, etc.[21]

It was to be shown, however, in the same year as that in which the dimorphism of sulphur was recognised (1823) that even the chemical properties can change without alteration of composition. In the analysis of fulminic acid, Liebig obtained numbers which agreed exactly with those established for cyanic acid.[22] This was at first believed to be an error, but subsequent examination confirmed the observation, and the great difference between the two substances seemed wholly inexplicable. Two years later, Faraday discovered another fact of the same kind.[23] He was engaged in the examination of oil·gas, when he discovered a hydrocarbon that behaved very like ethylene; but it did not yield chloride of carbon when mixed with chlorine and exposed to sunlight, and it possessed, moreover, a density double that of ethylene.[24] Further, an investigation of phosphoric acid was made at this period by Clark, who, through neglecting the fact that the salts contained water, was led to the opinion that there were two phosphoric acids, with different properties but with the same composition.[25] Berzelius had previously observed the same thing with respect to stannic acid.[26] He also showed in 1830 that the acid produced along with tartaric acid during the manufacture of the latter, had the same composition as tartaric acid. He calls the new substance racemic acid (*Drufsyra. Traubensäure*), and introduces the word isomer to designate substances of this kind. According to him, this word is only to be applied to compounds possessing the same composition and the same atomic weight, but with dissimilar properties.[27] A year later, Berzelius designates as polymerism the phenomena observed by Faraday respecting the hydrocarbons. This name embraces those cases where the same composition is accompanied by dissimilar properties and different atomic weights.[28] Metameric substances, on the other hand, are those which possess the same composition, the same atomic weight, and dissimilar properties, when the difference can be explained by a different arrangement of the atoms—*i.e.*, by a different constitution.[29] As an example, Berzelius very appropriately chooses stannous sulphate and stannic sulphite, which he writes: $SnO + SO_3$ and $SnO_2 + SO_2$.

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[21] Ann. Chim. [2] **24**, 264.

[22] Ibid. [2] **24**, 294; **25**, 288; Schweigger's Journal. **48**, 376.

[23] Phil. Trans. 1825, 440; Ann. Phil. **27**, 44 and 95; Schweigger's Journal. **47**, 340 and 441.

At that time, the different modifications of an element were also regarded as cases of isomerism; and it was only in 1841 that Berzelius introduced the word allotropy to designate such cases.[30] A number of examples belonging to this class were already known ; one of the most interesting being carbon, in the forms of diamond, graphite, and soot.

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[24] I mention here, in passing, that Faraday on the occasion of this investigation also discovered benzene. [25] Edinburgh Journal of Science. 7, 298; Schweigger's Journal. 57, 421. [26] Ibid. 6, 284. [27] Pogg. Ann. 19, 305. [28] It appears from this that Berzelius at that time regarded the vapour densities of compounds also as a guide to their atomic weights. [29] Berzelius, Jahresbericht 1833, 63.

It will be understood that the idea of metamerism could only be introduced after it had become possible to entertain any conception of the constitution of a substance ; while, on the other hand, the phenomena of isomerism necessarily led chemists to hypotheses respecting the mode of arrangement of the atoms. It is well known that there was in existence at that time a mode of regarding the facts which Berzelius endeavoured to extend more and more. I refer to dualism, which I have already had occasion to mention several times, and the consequences of which I shall now state more definitely.

The phenomena of combustion had led Lavoisier to assume, in so far as it was possible to do so, that substances consisted of two parts. This way of regarding them was very advantageous and clear in the case of salts, which were looked upon as composed of base and acid. This view was in agreement with their whole behaviour, and rendered it possible to consider them all from one common standpoint. The arguments of Gay-Lussac and Thenard against the elementary nature of chlorine, which have been stated in a previous lecture,[31] prove how deeply these ideas had become rooted, and how firmly it was the custom to base conclusions upon them.

After the existence of the so-called hydrogen acids (*i.e.*, of acids which do not contain oxygen) had been generally admitted, various opinions arose respecting the nature of their salts. A few investigators (Davy and Dulong, for example) regarded them as compounds of metals, just as they regarded other salts ;[32] but this view met with little approval at that time. Others remained true to the earlier conception, and with them common salt was still muriate of soda, which had the peculiarity, however, that it gave off its "water." Others, again, no longer looked upon these substances as salts, but compared them with the oxides. In this connection, the double chlorides and iodides prepared in 1826 by Boullay, caused the latter to develop his ideas more fully.[33] In accordance with these ideas, the chlorides, iodides, etc., of the alkali metals were bases, from which true salts were only produced by combination with the chlorides and iodides of the heavy metals; and the latter, in turn, were analogous with the acids. Others still, and amongst them Berzelius,[34] whose opinion at that time carried the greatest weight, regarded common salt and similar substances as compounds possessing a salt-like character; but they separated them from ordinary salts. According to them, the whole group of salts consisted of two divisions—the amphid salts, to which the oxygen, sulphur, etc., salts belonged, and the haloid salts, which embraced the chlorides, iodides, etc. The latter were composed of two elements or radicals—of a metal and a halogen, as chlorine, iodine, cyanogen, etc., at this time came to be called. It remained, however, altogether unexplained why substances with such similar properties as those of the amphid salts and the haloid salts, possessed such different constitutions.

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[30] Berzelius, Jahresbericht 1841, Part II. 13.

[31] See p. 81.

[32] See p. 83.

If it was desired to regard the oxygen salts as compounds of an acid with a base, then the establishment of these ideas was further attained as follows. Taking nitre as an example, KO would represent the base, and N_2O_5[35] the acid (or what we now call the anhydride). It thus came about that acetic acid was represented by $C_4H_6O_3$, formic acid by $C_2H_2O_3$, sulphuric acid by SO_3, etc.; that is, instead of the actually existing substances, others were represented, of which some were imaginary. The free acids were held to contain "a proportion of water which we cannot separate except by combining the acid with another substance";[36] and although Berzelius himself had previously distinguished water of hydration from water contained in salts and not necessary for their existence,[37] yet this water also was neglected, as if non-existent, in most of the discussions as to the constitution of bases and acids. It may have been a consequence of this that the presence of water was assumed even in substances which belonged to other classes, when hydrogen and oxygen were found in them in the proportions necessary to form water, and that this water was then neglected in writing formulæ for these substances. Many things might be adduced as having contributed to erroneous ideas of this kind; such, for example, as the way in which Gay-Lussac and Thenard in 1811 interpreted their analytical results relating to organic substances.[38] According to these chemists, substances fall naturally into (1) those which contain just as much oxygen as is required in order to form water with the hydrogen present (carbohydrates); (2) those which contain less (resins, oils); and (3) those which contain more (acids).

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[33] Ann. Chim. [2] **34**, 337; Journ. de Pharm. **12**, 638.

[34] Berzelius, Lehrbuch. Third Edition, **4**, 6.

[35] Berzelius' atomic weights: see p. 100.

[36] Berzelius, Lehrbuch. Third Edition, **2**, 4.

[37] Journ. de Phys. **73**, 253.

I regarded these perhaps seemingly detailed explanations as necessary, before I could enter more minutely into the views respecting the constitution of organic compounds. In passing on now to this most important question, I wish to show how dualism was gradually introduced here also, and how the radical theory arose as a consequence of this.

Berzelius explained in 1819 that his electro-chemical theory could not be extended to organic chemistry, because under the influence of the vital force the elements there possessed entirely different electro-chemical properties. In decay, putrefaction, fermentation, etc., he observes phenomena which he regards as demonstrating the tendency of the elements to return to their normal condition.[39] He did not, at that time, as yet consider it possible to regard all organic substances as binary groups. Dualism was, indeed, extended as far as possible; the oxygen compounds were looked upon as "oxides of compound radicals, which, however, do not exist free, but are wholly hypothetical,"[40] a mode of regarding the matter which was especially applicable to the acids. Accordingly, we now hear the radicals of acetic acid, C_4H_6, of benzoic acid, $C_{14}H_{10}$, etc., spoken of, and these radicals are the remainders of the acids after the deduction of their oxygen.

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[38] Rech. phys. chim. **2**, 265. [39] Essai etc., 96. [40] Berzelius, Lehrbuch, First Edition, **3**, Part I. 149.

It is easily understood that endeavours should be made from other points of view, and in other directions, to establish hypotheses regarding the nature of organic substances ; but I may pass over those which possessed no general significance and were applicable to a few substances only. I must, however, adduce one example of this kind, because the idea involved was for a long time held in respect in chemistry. It has to do with a conception of oxalic acid, which was then written C_2O_3, the elements of water being neglected. Döbereiner, who carefully studied the behaviour of the oxalates in 1816, proved that some of them give off carbonic anhydride and carbonic oxide when heated, and on this account he thought himself justified in regarding the "acid of sorrel" as carbonate of carbonic oxide.[41] This was an attempt to refer back complex substances to simpler ones, and it possesses a certain significance, in so far that it is based upon facts.

More important by far is an observation of Gay-Lussac's concerning the composition of alcohol and of ether, which dates from about the same time,[42] and which became the basis of the so-called Etherin Theory. The discoverer of the law of gaseous volumes points out that the densities of the vapours of alcohol, ether, and water, and the density of olefiant gas, stand to each other in such a relation that ether may be regarded as composed of half a volume of water vapour and one volume of olefiant gas, and alcohol as composed of equal volumes of the two.

Dumas and Boullay adopted this observation as the basis of the views regarding the ethereal compounds, which they advanced in 1828 on the occasion of a detailed investigation of these substances.[43] In their view olefiant gas is a radical ; that is, a group of atoms which enters into combinations in the same way that the elements do. They compare it with ammonia, and are at pains to show that, just as the latter is the radical of the ammonium salts, olefiant gas must be assumed in the ethers. In doing so, they try to carry the analogy so far that they even assert that ethylene possesses basic properties, and that the reason why it does not colour litmus tincture blue is merely because it is insoluble in water ; and that its alkaline nature is proved, moreover, by its property of neutralising hydrochloric acid, whereby hydrochloric ether, observed so long ago by Basil Valentine, is produced. They then show, by means of a table, how the radical C_4H_4 or $2C_2H_2$ (olefiant gas) may be assumed in the formulæ of the ethers analysed by them ; whereby complete uniformity with the ammonium salts is attained :—[44]

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[41] Schweigger's Journal. **16**, 105.

[42] Ann. Chim. **91**, 160 ; **95**, 311.

[43] Ibid. [2] **37**, 15.

Olefiant Gas - - -	$2C_2H_2$	NH_3 - - - -	Ammonia
Hydrochloric Ether -	$2C_2H_2+HCl$	NH_3+HCl - -	Sal-ammoniac
Ether - - -	$4C_2H_2+H_2O$		
Alcohol - -	$4C_2H_2+2H_2O$		
Acetic Ether	$4C_2H_2+C_8H_6O_3+H_2O$	$2NH_3+C_8H_6O_3+H_2O$	Acetate of Ammonia
Oxalic Ether	$4C_2H_2+C_4O_3+H_2O$	$2NH_3+C_4O_3+H_2O$	Oxalate of Ammonia, etc.[45]

We find the opinion that the ethers are to be regarded as analogous to salts, first advanced by Dumas and Boullay, although it is true that they did not adopt the usual view, in accordance with which salts do not contain any water. The endeavour to classify the organic compounds in the same way as the inorganic ones, constituted the basis of their views, however ; and, since this idea was found to be applicable to a whole class of substances, it was thus of great importance. The point of view was distinctly dualistic, but not quite in the former sense. Accordingly we find that Berzelius at first maintains a very cautious attitude towards it ;[46] he finds in it at best a symbolic mode of expression, which cannot be regarded as representing the actual composition of the substances. Only some years afterwards does he revert, for a short time, to Dumas' ideas, and he then calls the radical C_4H_8 Etherin.[47]

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[44] Here, as in all other cases, I quote the formulæ of the authors, and hence I employ in this case Dumas' atomic weights which are referred to $H=1 : O=16, C=6$, etc.

[45] The table given in the paper quoted above contains obvious misprints ; compare Dumas, Traité. Organic Part, I, 68.

[46] Berzelius, Jahresbericht 1829, 286.

This appears to me to be the place to state the results of an investigation of Gay-Lussac's into the cyanogen compounds, which had been carried out as early as 1815, and contributed materially to giving a more definite meaning to the conception of a radical.[48] Gay-Lussac repeated Berthollet's experiments on the composition of hydrocyanic acid and confirmed them, inasmuch as he established beyond all doubt that the acid is free from oxygen, and contains carbon, nitrogen, and hydrogen only. The examination of the salts led him to study the behaviour of mercuric cyanide at high temperatures, and thus to discover cyanogen. What is of importance for us in Gay-Lussac's work, is the way in which he regards the substances he describes. These are, in his view, compounds of a radical containing carbon and nitrogen (cyanogen) and identical with the gas obtained from mercuric cyanide. The possibility of preparing radicals was in this way demonstrated, and, in consequence, the conception attained a more real significance. It is further to be remarked that Gay-Lussac, in calling the radical of hydrocyanic acid, cyanogen, permitted himself a certain freedom, since it was not actually "the residue of an acid which has been deprived of its oxygen." Obviously the great French scientist compares hydrocyanic acid with hydrochloric acid, and with hydriodic acid which he had himself discovered a short time previously. They are hydrogen compounds of elements or radicals, exactly as the ordinary acids are oxygen compounds. If it was now desired to define a radical, and to include cyanogen in the definition, it was no longer possible to say, with Lavoisier, that "it is the residue of a substance which has been deprived of its oxygen"; but it was the other half of the definition that was to be accentuated; "a radical is a composite group which behaves like an element."[49] As a consequence of Gay-Lussac's investigation, and of the isolation of cyanogen, this latter view had acquired an increased significance. Reflections of a similar kind do not appear to have occurred further to the chemists of that period. Generally speaking, radicals were only looked for in oxygen compounds, and especially in acids; whereas Dumas and Boullay's assumption of Etherin proves, on the other hand, that attention was not confined exclusively to these.

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[47] Annalen. 3, 282. [48] Ann. Chim. 95, 136.

Wöhler and Liebig's investigation of bitter almond oil and its derivatives, in 1832,[50] had a pronounced effect on the views respecting radicals. It led these two chemists to the assumption of a radical containing oxygen, and thus added an entirely new significance to these ideas.

Wöhler and Liebig first show that the conversion of bitter almond oil into benzoic acid consists in the taking up of oxygen, since they establish the formulæ $C_{14}H_{12}O_2$ and $C_{14}H_{12}O_4$ respectively for the two substances.[51] In doing so, they assume, however, an atom of water, H_2O, in the latter; but they neglect this and write the formula of benzoic acid $C_{14}H_{10}O_3$. In this way they come to look upon both substances as compounds of the radical Benzoyl, $C_{14}H_{10}O_2$, and to regard bitter almond oil as benzoyl hydride, and benzoic acid as an oxygen compound of the new radical. They show, in the course of the investigation, how the same radical may likewise be assumed in an extensive series of substances. By treatment of bitter almond oil with chlorine and bromine, they prepare benzoyl chloride and bromide, $C_{14}H_{10}O_2.Cl_2$ and $C_{14}H_{10}O_2.Br_2$. From these, by means of potassium iodide and of potassium cyanide, they obtain the iodine and the cyanogen compounds of the radical, $C_{14}H_{10}O_2.I_2$ and $C_{14}H_{10}O_2.Cy_2$. Finally, with ammonia and with alcohol, they obtain benzamide and benzoic ether.

This investigation is regarded even now as one of the greatest achievements in the range of organic chemistry. The impression which it produced at the time can be well understood. It was the first instance where, starting from one compound, an extensive series of well-defined substances had been obtained, the relations of which could easily be explained if the suggested mode of regarding them was adopted. We thus find Berzelius, then at the zenith of his fame and only seldom in accord with the views of others, bestowing abundant praise upon the investigation.[52] He hopes that, as a consequence of it, a new day will dawn in chemistry, and he proposes to Liebig and Wöhler to call the new radical Proin or Orthrin (break of day) because he believes that a clearer light will be cast upon our science by the assumption of ternary radicals.

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[49] Lavoisier, Oeuvres. 1, 138.

[50] Annalen. 3, 249.

[51] Berzelius' atomic weights.

And Berzelius was right! For even although the chief importance of the investigation does not rest with the radical composed of three elements, still the special part which had been universally attributed to oxygen since Lavoisier's time, even in this branch of chemistry, was taken away from it. Further, that the true signification of the word radical was to be sought for elsewhere, was demonstrated by the fact that, in the choice of a radical, the composition was left entirely out of consideration; and the justification of this proceeding was found in the experimental results. Benzoyl was a radical because, like an element, it combined with other elements, and because it could be transferred, without decomposition, from the compounds so formed, into others. It was the key to the interesting reactions of Liebig and Wöhler, and it formed the foundation of the benzoic acid series just as cyanogen was the basis of a large number of substances.

Cyanogen and benzoyl are the pillars of the radical theory, which received confirmation by the discovery of cacodyl. I cannot enter into the details of this extremely difficult and brilliantly executed investigation of Bunsen's, but it is my duty to state the general results of his work.

In 1760, Cadet had obtained a fuming liquid, possessing a nauseating smell, by distilling potassium acetate with arsenious anhydride.[53] This liquid took fire spontaneously in air, and it was known to contain arsenic and to be poisonous. These properties appear to have deterred chemists from the study of it, for, with the exception of a few unimportant experiments by Thenard, they had not occupied themselves with it at all for seventy years, and had been content to mention it in text-books as Cadet's liquid. Dumas had then endeavoured, by distillation, to separate a pure compound from the crude product, which was contaminated, amongst other things, with elementary arsenic. According to his analyses, it is represented by the formula $C_8H_{12}As_2$ [$C=6$, $As=75$].[54] Bunsen's first results appeared to confirm this,[55] while later experiments eventually fixed it as $C_4H_{12}As_2O$ [$C=12$].[56] Bunsen called the substance cacodyl oxide, and assumed the existence in it of the radical $C_4H_{12}As_2$. He succeeded in preparing the chloride, bromide, iodide, cyanide, and fluoride by treatment with the corresponding acids; the action of barium hydrosulphide produced the sulphide; by oxidation Bunsen obtained cacodylic acid, $C_4H_{12}As_2.O_3+H_2O$; finally, he found it possible to isolate the radical cacodyl by decomposing the chloride by means of zinc, and, naturally, this assisted very materially in procuring recognition for his mode of regarding the matter. We can understand how keenly interest must have been aroused on hearing of the isolation of an organic radical containing a metal, and possessed, besides, of the extremely remarkable property of spontaneous inflammability.

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[52] Annalen. 3. 282.

I have intentionally introduced here the account of this important research of Bunsen's (the completion of which falls at a later date) in order to be able to make clear the idea of a radical as it now gradually came to be conceived. This idea is essentially different from what was formerly understood by the term, and the new conception was brought to the front by means of a series of investigations, of which I have shortly stated the most important. In doing this, I was at pains to explain the development of the ideas, and I only desire now to be permitted to define the meaning of the term as it eventually became fixed in the minds of the chemists of the period.

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[53] Mém. de Math. et de Phys. des savants étrangers. **3**, 633. [54] Dumas, Traité. Organic Part, **1**, 135; compare Annalen. **27**, 148. [55] Annalen. **24**, 271. [56] Ibid. **31**, 175; **37**, 1; **42**, 14; **46**, 1.

I begin with the celebrated definition of Liebig:[57] "We call cyanogen a radical," he says, in 1837, in his criticism of Laurent's theory, "(1) because it is a non-varying constituent in a series of compounds, (2) because in these latter it can be replaced by other simple substances, and (3) because in its compounds with a simple substance, the latter can be turned out and replaced by equivalents of other simple substances."

These three requirements, of which, according to Liebig, at least two must be fulfilled in order that an atomic group may have any claim to the designation of radical, prove that only a study of the nature of a compound could lead to a knowledge of the radical contained in it. The behaviour of a substance towards elements and compound bodies required to be known, in order that its radical might be ascertained; and from this it may be gathered what significance such a determination possessed. The choice involved, to a certain extent, a résumé of the whole investigation, since the decomposition products were known when the radical was known; the latter was, of course, composite itself, but with its decomposition, those affinity relations ceased which connected with one another, substances containing the same radical. That the radical behaved like an element, had been confirmed over and over again. Not only did it enter into combinations with elements, but it could also be isolated from these combinations. How far this comparison was carried, is shown by a quotation taken from a joint paper by Dumas and Liebig:[58] "Organic chemistry possesses its own particular elements, which sometimes play the part taken by chlorine and oxygen in inorganic chemistry; sometimes, on the other hand, the part of the metals. Cyanogen, amide, benzoyl, the radicals of ammonia, of fatty bodies, of alcohols and analogous bodies, these are the real elements with which organic chemistry operates, and not the ultimate elements carbon, hydrogen, oxygen, and nitrogen, which only appear when every trace of organic origin has disappeared." It will thus be understood that the atoms which constituted such a group were supposed to be held together by stronger forces than those which united the group to other atoms. The radical in this way attained a very real significance in the minds of the chemists of that period; it actually existed in the compound, and hence, in any particular substance, only a single radical could be assumed since there was only one present. And thus, with the constantly increasing importance which the radical of a substance attained in respect to views concerning its constitution, divergences necessarily arose in the choice of a radical, according to the decomposition products which were looked upon as the most important. The discussions thus called forth were very helpful in the further development of the science. Everyone tried to support his own view by evidence, and this could only be found in the reactions of the substance. We are indebted to these discussions, therefore, for a very intimate knowledge of certain classes of substances.

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[57] Annalen. **25**, 3.

[58] Comptes Rendus. **5**, 567.

The foregoing explanations will not, I hope, prove superfluous. Their purport is to render clear the importance of the radical theory, the further development of which will be discussed in the next lecture.

LECTURE VIII.

FURTHER DEVELOPMENT OF THE RADICAL THEORY—VIEWS CONCERNING ALCOHOL AND ITS DERIVATIVES—PHENOMENA OF SUBSTITUTION — DUMAS' RULE — THE NUCLEUS THEORY — THE EQUIVALENT OF NITROGEN.

IN the preceding lecture I endeavoured to explain the significance of the radical, and I shall now deal more fully with its nature. Enough has been said already by way of preparation for the controversies which were called forth by the choice of a definite atomic group as the radical of a compound ; and I now consider it my business to pass in review the most important of the discussions. It was especially with respect to the constitution of alcohol, and of the substances derived from it, that differences of opinion arose. Since it cannot be denied that the opinions regarding these compounds exercised an important influence upon general views, and, further, since the most prominent chemists took part in the discussions, I shall endeavour to show, with respect to this group of substances, how various and how contradictory were the conceptions as to the arrangement of the atoms.

I dealt, in the preceding lecture, with the so-called etherin theory, which originated in the comparison of the ethers with the salts of ammonia. In that comparison the radical NH_3 was assumed to be present in these salts ; and even although the dualistic tendency of the whole mode of regarding them cannot be disputed, still the view is not in harmony with the other opinions respecting salts. Even then there was another theory as to the compounds of ammonia, in accordance with which they did not occupy any exceptional position, but were looked at from a purely dualistic point of view.

The radical ammonium, which, as has already been stated, was introduced into the science by Davy,[1] constitutes the basis of this hypothesis. Ampère[2] and Berzelius[3] were afterwards chiefly instrumental in procuring its recognition. The superiority of this view, with its purely dualistic basis, as compared with the other, is indisputable; for the compounds of ammonia (ammonium compounds) now appear as analogues of the ordinary salts, as their behaviour necessarily requires that they should. The analogy was illustrated thus:—[4]

Sal ammoniac - -	$(N_2H_8)Cl_2$	KCl_2 - -	Muriate of Potash
Sulphate of Ammonia	$(N_2H_8)OSO_3$	$KOSO_3$ - -	Sulphate „
Nitrate „	$(N_2H_8)ON_2O_5$	KON_2O_5 -	Nitrate „
Acetate „	$(N_2H_8)OC_4H_6O_3$	$KOC_4H_6O_3$ -	Acetate „

It is clear that this way of regarding substances could also be applied to the compound ethers, if the radical C_4H_{10} were assumed instead of C_4H_8. Berzelius took this step in 1833.[5] He was led to do so not only by his predilection for the ammonium theory, but also on account of newly discovered facts which I shall state here.

During the same year, Magnus, by acting with sulphuric anhydride on alcohol and ether, had discovered ethionic and isethionic acids.[6] The latter acid was obtained by the decomposition of the former by means of water, and, according to the analyses, it was isomeric with it. Its barium salt, in accordance with the prevailing etherin theory, had the formula $C_4H_8 + 2SO_3 + BaO + H_2O$ assigned to it; or, according to Magnus, it was to be regarded as a compound of ether and anhydrous sulphuric acid, with baryta. Liebig and Wöhler's analyses of barium sulphovinate,[7] which were confirmed by Magnus,[8] had fixed its composition as $C_4H_8 + 2SO_3 + BaO + 2H_2O$;

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[1] See p. 76. [2] Ann. Chim. [2] **2**, 16, Note. [3] Gilb. Ann. **46**, 131; Berzelius, Lehrbuch. Third Edition. [4] Berzelius adopts NH_4 as an atom of ammonium; and yet this does not occur in combination any more than an atom of ammonia NH_3. Instead of it the double atom ~~NH~~$_4$ $(=N_2H_8)$ always occurs. The isomorphism of ammonium chloride and potassium chloride must have influenced him to write ~~NH~~$_4Cl_2$ and not $(NH_4)_2Cl_2$. [5] Pogg. Ann. **28**, 626. [6] Annalen. **6**, 152. [7] Ibid. **1**, 37. [8] Magnus, *loc. cit.*

that is to say, it seemed to contain an atom of water more than the newly discovered compound. Berzelius now draws attention to the fact that the latter compound cannot be converted into the barium salt of sulphovinic acid by boiling it with water, and that therefore the view underlying these formulæ (in accordance with which the substances contain ready formed water) is erroneous. According to him, alcohol and ether are the oxides of two radicals, C_2H_6 and $\cancel{C}_2\cancel{H}_5 = C_4H_{10}$. The compound ethers are thus still regarded as composed of ether and of acid; but there is no longer ready formed water in them, and they now become comparable with salts:—

Ether - -	- $C_4H_{10}O$	KO - -	- Potash
Haloid Ether - -	$C_4H_{10}Cl_2$	KCl_2 -	- Muriate of Potash
Acetic " -	$C_4H_{10}O + C_4H_6O_3$	$KO + C_4H_6O_3$	- Acetate "
Nitric " -	$C_4H_{10}O + N_2O_5$	$KO + N_2O_5$	- Nitrate "

Berzelius very clearly perceived the importance of his suggestion. He had now attained what he had long striven for. The dualistic conception was now applicable to organic compounds, or at least to the most fully investigated group of them; and he does not conceal the pleasure which this occasions him. He states that the organic substances are now to be regarded (in the same way as mineral substances) as binary groups, but that in them compound radicals alone play the part of the inorganic elements—a view which Dumas and Liebig afterwards develop fully in a special treatise.[9] (Compare p. 128.)

A ground for discord was now provided, and it was not to be long before the contention should begin. The next incitement to it is given by Liebig, who throws down the glove to the etherin theory.[10] According to him, this theory has no justification, and all the grounds that can be advanced in its favour rest upon fallacious experiments. Amongst these there is, in the first place, an observation of Hennell,[11] according to which sulphuric acid absorbs etherin (olefiant gas) and produces sulphovinic acid directly. Liebig endeavours to prove that Hennell's etherin was contaminated with the vapours of alcohol and of ether, and that the pure gas is not absorbed by sulphuric acid.[12] He then attacks the formulæ of Zeise's platinochloride compounds, which, according to their discoverer, consist of etherin, platinous chloride, and potassium chloride.[13] Liebig thinks he is justified in concluding from Zeise's analyses, and from the reactions of the substances, that it is not etherin but ether that they contain. Finally, he disputes the existence of the ethyl-oxalate of ammonia (ethyl-oxamate) which Dumas and Boullay had prepared from oxalic ether and dry ammonia gas.[14] According to Liebig, the same substance is formed by the action of aqueous ammonia, and is identical with oxamide. By this attack all the supports of the etherin theory seemed to be destroyed. Liebig, in bringing the matter forward, admits his adherence to the hypothesis of Berzelius regarding the ethereal compounds, while he only differs from him in his view with respect to alcohol. In the latter substance also he assumes the radical C_4H_{10}, which he calls ethyl; and with him alcohol is the hydrate of ether, $C_4H_{10}O,H_2O$. In Liebig's opinion it was no objection that half as many atoms were thus assumed in one volume of alcohol as were assumed in the same volume of ether. Chemists were now further than ever from adopting Avogadro's hypothesis, as may be gathered from the following assertions of Liebig :—[15]

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[9] Comptes Rendus. 5, 567. [10] Annalen. 9, 1. [11] Phil. Trans. 1826, 240; 1828, 365.

"Apart from the contradiction which is involved, if ether as an oxide is deficient in the property of uniting with water to form a hydrate, while, like other oxides, it is able to unite with acids, and like the metals, its radical is able to unite with the halogens, the specific gravity of alcohol vapour cannot be looked upon as any evidence for its constitution as an oxide of another radical. On the contrary, I believe the very circumstance that ether and water vapour unite in equal volumes, and without condensation, is evidence in favour of the view that this compound, alcohol, is a hydrate of ether. . . . In the formation of benzoic ether from absolute alcohol and benzoyl chloride, we perceive a simple decomposition of water, which does not extend further than to the water of hydration."

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[12] Berthelot afterwards showed that absorption can be brought about by vigorous shaking. [13] Mag. f. Pharm. **35**, 105; Pogg. Ann. **21**, 533. [14] Ann. Chim. [2] **37**, 15. [15] Annalen. **9**, 16.

Liebig went too far in his argumentation, and Zeise and Dumas justly protested against it. The former repeats his previous examination of the inflammable platinochloride, and finds his first results confirmed: there is no more oxygen present in the compound from which the water of crystallisation has been removed, and, therefore, ether cannot be assumed to be present in it, but only etherin.[16] Dumas likewise upholds his earlier experiments.[17] He points out the difference in the action of aqueous and of dry gaseous ammonia upon oxalic ether. In the first case only is oxamide formed, whereas ammonia gas gives rise to the substance he had previously described, which he now calls oxamethan, and to which he assigns the formula C_4O_3,NH_3,C_4H_4 [$C = 6$].[18] As a consequence, Dumas also adheres to his old opinion. He draws attention likewise to the fact that it was with him the idea originated according to which ordinary ether ("sulphuric ether") is the base of the compound ethers; and he states that it is, in point of fact, the essence of the whole ethyl theory. He goes a step further, indeed, inasmuch as he regards ether itself as composed of water and olefiant gas.

In this Dumas was right. There was one point, however, which had previously been brought forward by Liebig,[19] on which Dumas and Liebig differed. This was the assumption by Dumas that in ether two of the hydrogen atoms play a different part from the others; and Liebig contested this particular point. The discovery of the mercaptans by Zeise[20] furnishes Liebig with an opportunity to adduce new proofs of the accuracy of his ideas.[21] He regards these compounds as analogous to alcohol; they are composed of ethyl sulphide, $C_4H_{10}S$, and sulphuretted hydrogen, H_2S, and their extremely interesting metallic compounds show that in them there really are two hydrogen atoms which behave differently from the others. Two years later, in 1836, he collects together all the grounds for and against each view;[22] and from the most various facts (but especially from the phenomena of substitution, already discovered by Dumas), he considers himself justified in drawing the conclusion that ether is not a hydrate but an oxide.

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[16] Annalen. **23**, 1. [17] Ann. Chim. [2] **54**, 225. Annalen. **10**, 277; **15**, 52. [18] It seems as if Dumas, in accordance with his earlier experiments assumed one atom of water more; the analyses do not, however, afford any sharp decision respecting this. [19] Annalen. **9**, 15. [20] Ibid. **11**, 1.

The matter was not yet settled, however. In his examination of wood spirit (carried out in conjunction with Peligot), Dumas had found new support for his views.[23] He succeeded in settling the composition of this substance, a matter that different chemists had attempted to settle, but without success. He showed that in its whole behaviour it had the closest resemblance to alcohol, forming, as the latter does, ethereal compounds with acids; and he assumes in it the radical C_2H_4, methylene, with which etherin is polymeric. The advantages of this way of regarding the matter, which does not lead to the assumption of hypothetical radicals, are again pointed out.[24]

The discussion between Berzelius, Dumas, and Liebig, of which I have given some examples, was of much service to our science. The facts were illuminated from the most different points of view, and this was far more favourable for progress than if a single theoretical opinion had come too prominently to the front. The chemists just mentioned were the chief exponents of chemistry at that time, and round them the other investigators gathered. Of these, only a few represented independent opinions, and chemists were divided, accordingly, into three camps. It is true that in 1837 a sort of armistice was concluded. At a personal interview, Liebig converted Dumas to his opinions, and we find the two savants conjointly publishing a scientific treatise[25] in which they announce that thenceforth they wish to elaborate organic chemistry with united energies and from the same point of view ; to have analysed in their laboratories all the substances not yet examined by them ; to open up, by the aid of their pupils, additional lines of investigation in the most varied directions ; and to subject the work of others to a rigid criticism and check. But the union only endures for a short time : it is terminated in a year, and each returns to special paths, which diverge more and more. In 1840 the two are again hostile towards each other, although perhaps more careful in their assertions and more polite than previously.

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[21] Annalen. **11**, 10. [22] Ibid. **19**, 270, Note. [23] Ann. Chim. [2] **58**, 5; Annalen. **13**, 78; **15**, 1. [24] Dumas and Peligot believe that they can isolate methylene.

Dumas had made observations in the meantime which caused him to break away from all traditions, to abandon dualism and the electro-chemical theory, and to express views that Berzelius especially attacked most vigorously. The latter, who up to this time had taken the most important part in the development of the science, holding his opponents in check by means of his theories, and who had struggled for the ascendency with Liebig and Dumas, now tries, ineffectually, to oppose his ideas to those of Dumas and of Laurent. He relies upon unestablished hypotheses, which only later, at Kolbe's hands, receive a real foundation, and acquire thereby a scientific significance.

Before turning to this period, with its theories of substitution, of nuclei, and of copulæ, we must still consider a further development of radicals in the earlier sense, with which the various notions respecting alcohol and the compounds derived from it are brought to a close.

Regnault, in his examination of the oil of the Dutch chemists, had found that this substance loses the elements of hydrochloric acid when it is distilled with potassium hydroxide, and that it yields a new substance of the composition $C_4H_6Cl_2$.[26] This he regards as the chloride of the radical aldehydene, C_4H_6, and confirms his view by preparing the bromine and iodine compounds of this radical, which he also assumes to be present in aldehyde and in acetic acid. He writes :—

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[25] Comptes Rendus. 5, 567. [26] Ann. Chim. [2] 59, 358 ; Annalen. 15, 60.

C_4H_6 - - -	Hypothetical radical Aldehydene
C_4H_6,Cl_2 - -	Chloraldehydene
C_4H_6,Br_2 - -	Bromaldehydene
$C_4H_6,Cl_2 + H_2Cl_2$ -	Chloride of Hydrocarbon (Ethylene chloride)
$C_4H_6,Br_2 + H_2Br_2$ -	Bromide of Hydrocarbon (Ethylene bromide)
$C_4H_6,O + H_2O$ -	Aldehyde
$C_4H_6,O_3 + H_2O$ -	Acetic acid

This investigation of Regnault's, carried out in 1835, was prompted by Liebig, and was intended to prove to Dumas that the radical etherin is not present even in ethylene chloride ; it was intended to overthrow the etherin theory, and it may have had much influence in moving Dumas to give up his former views. It is true that in consequence of this investigation Liebig also abandoned the radical ethyl, and tried to explain the ethereal compounds on the assumption of a radical acetyl, C_4H_6.[27] These substances are again compared with the salts of ammonia, but in the latter the radical amide is now assumed.

Acetyl - - -	$Ac = C_4H_6$	$Ad = N_2H_4$ -	Amide
Olefiant gas - - -	AcH_2	AdH_2 - -	Ammonia
Ethyl - - - -	AcH_4	AdH_4 - -	Ammonium
Ether - - - -	AcH_4O	AdH_4O - -	Ammonium oxide
Ethyl chloride - -	AcH_4Cl_2	AdH_4Cl_2 -	Sal ammoniac
Alcohol - -	$AcH_4O + H_2O$	$AdH_4O + H_2O$	Compound in sulphate of ammonia
Mercaptan - -	$AcH_4S + H_2S$	$AdH_4S + H_2S$	Hydrosulphuret of ammonia
Isethionic acid - -	$AcH_2 + 2SO_3$	$AdH_2 + SO_3$ -	Rose's anhydrous sulphate of ammonia.
Acetic acid - -	$AcO + O_2$		
Aldehyde - - -	$AcO + H_2O$		

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[27] Annalen. **30**, 139.

Three views respecting the ammonium salts and the compound ethers had thus been advanced, and these differed from one another merely in the number of hydrogen atoms which were assumed in the radical. These were :—

1. The ammonia theory of Lavoisier, corresponding to the etherin theory of Dumas and Boullay;
2. The ammonium theory of Davy, Ampère, and Berzelius, corresponding to the ethyl theory of Berzelius and Liebig; and
3. The amide theory of Davy and Liebig, corresponding to the acetyl theory of Regnault and Liebig.

Liebig believed that, by his new theory, he had overcome all difficulties, and had settled all contentions with respect either to the ethyl theory or the etherin theory. He closes his paper with the following words: "From this point of view, both of the formerly opposed theories possess, as may easily be observed, the same kind of basis, and all further question as to the truth of the one view or of the other is thereby settled."

In a certain respect, Liebig was right; the question whether ethyl or etherin was present in alcohol was no longer discussed; not, perhaps, because acetyl was preferred, but because chemists now began to attach another signification to the radicals. The phenomena of substitution, which were already known, gradually became of general applicability, and, after the discovery of trichloracetic acid, the hypotheses which Dumas and Laurent had advanced, acquired great influence. Not only was the radical theory, in the form in which it was then stated, threatened by these hypotheses, but dualism and the electro-chemical theory—the very foundations of the entire mode of viewing chemical matters—were attacked by them, and were eventually driven out of the science. These hypotheses led to the recognition of the radicals as variable and of chemical compounds as possessed of an individual or unitary character; and to the abandonment, as arbitrary, of the division of the latter into two parts. At a later period, in conjunction with the conceptions derived from the theory of the polybasic acids, they led to a revision of the size of the atoms in the case of compounds, to the establishing of the chemical molecule, and to the theory of types. Simultaneously, the conception of the equivalent assumes a more fixed form, and is distinguished from that of the atom ; it is recognised that the atoms are not equivalent, but are of different values in combination ; the theory of atomicity is developed and this stimulates the determination of rational constitution as we now understand it.

Let us next make something more than a mere bird's eye inspection of this period, rich as it is in discoveries and hypotheses. We shall now subject it to a minute examination. In doing so, we find that the development of chemistry during the last sixty years is not inferior in interesting and important episodes to that of any period in the science. The participation in this development is a constantly increasing one and it is a difficult task to seek out from the enormous mass of material which was elaborated during this period, the things that were important and conducive to progress, to state the development of the ideas in such a way that they shall be at once logical and in accordance with the actual facts, to do justice to every one, and yet not to lose the thread over details or questions of priority.

The history of this epoch has never yet been described in a connected manner.[28] In venturing upon the attempt to do this, I am well aware that an objective representation of the period is scarcely possible, and that I play the part rather of critic than of historian. Still I have endeavoured to make my exposition of some value from the fact that I have always been careful to arrive as nearly as I could at the truth, and not to permit myself to be led by prejudices or personal matters.

The conception of equivalence might have led to that of replacement or substitution, since the quantities of two acids were equivalent when they saturated the same quantity of a base. The acid in a neutral salt could thus be replaced by its equivalent, without the neutrality being interfered with. The word "replacement" received further justification after Mitscherlich had studied the phenomena of isomorphism. It could then be said that certain elements in a crystal might be replaced by others, without alteration of the crystalline form. Such substitutions possessed the peculiarity, however, that they were not connected with any proportions by weight, and it may thus appear all the more remarkable that they should render important assistance in the determination of atomic weights. The hypothesis underlying the phenomena of isomorphism was that one atom could only be replaced by one other; that is to say, that the numbers of the atoms in isomorphous compounds must be identical. Since chemically similar substances had alone been compared, an extension of the prevailing views, based on the phenomena of isomorphism, would have been quite possible; but this class of phenomena had never led to any attack upon the system.

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[28] Wurtz's Histoire des doctrines chimiques only appeared during the printing of the first edition of these lectures, and Kopp's Entwickelung der Chemie in der neueren Zeit appeared some years afterwards.

Such an attack now took place, however, and it was founded upon a series of facts which I must relate here. In the bleaching of wax by means of chlorine, Gay-Lussac had observed that for every volume of hydrogen eliminated, an equal volume of chlorine was taken up.[29] He had also found the same thing in the action of chlorine on hydrocyanic acid. In the course of their investigation of the benzoyl compounds, previously referred to, Wöhler and Liebig, when acting with chlorine upon bitter almond oil, had discovered benzoyl chloride; and they expressly remark that this substance is produced from the bitter almond oil by two atoms of chlorine taking the place of two of hydrogen.[30] In 1834, Dumas examines the action of chlorine on oil of turpentine,[31] and in this case also each volume of hydrogen eliminated is replaced by the same volume of chlorine. Then when he studies the products of the decomposition of alcohol by means of chlorine and of bleaching powder, in order to clear up the nature, and the mode of formation of chloral and of chloroform, he states the empirical rule, observed in a single case by Gay-Lussac, in the following general form:—[32]

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[29] Gay-Lussac, Leçons de Chimie. [30] Annalen. **3**, 263. [31] Ann. Chim. [2] **56**, 140. [32] Ibid. [2] **56**, 113.

1. When a substance containing hydrogen is exposed to the dehydrogenising action of chlorine, bromine, or iodine, for every volume of hydrogen that it loses, it takes up an equal volume of chlorine, bromine, etc.

2. When the substance contains water, it loses the hydrogen corresponding to this water without replacement.

The second rule was advanced chiefly to explain the formation of chloral, and at the same time to justify the formula $C_8H_8 + 2H_2O$ [$C = 6$] adopted for alcohol by Dumas six years previously. According to Dumas, the phenomena of substitution furnish a new proof of the difference of the hydrogen atoms, eight of which are united to carbon, and four to oxygen. In the case of the former alone does replacement occur, whilst the others are removed without replacement.

Thus we have :—

$$(C_8H_8 + 2H_2O) + 4Cl = \underset{\text{Aldehyde.}}{C_8H_8O_2} + 4HCl$$

$$C_8H_8O_2 + 12Cl = \underset{\text{Chloral.}}{C_8H_2Cl_6O_2} + 6HCl$$

By means of various examples, Dumas further endeavours to prove the general validity of the laws which he advances. In establishing the correct composition of the Dutch oil, he points out that the chloride of carbon obtained from it by means of chlorine, and examined by Faraday,[33] supplies a new argument in favour of the accuracy of his views. He also finds similar support in the action of chlorine on hydrocyanic acid, on bitter almond oil, etc.

But Dumas is not satisfied with this. He goes a step further still, and regards oxidations as cases of substitution, as, for example, the conversion of alcohol into acetic acid.[34] In this case every volume of hydrogen eliminated is replaced by half a volume of oxygen. Accordingly we have :—

$$\underset{\text{Alcohol.}}{(C_8H_8 + H_4O_2)} + O_4 = \underset{\text{Acetic Acid.}}{(C_8H_4O_2 + H_4O_2)} + H_4O_2\ ;$$

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[33] Phil. Trans. 1821, 47. [34] Ann. Chim. [2] 56, 143.

and the formation of benzoic acid from bitter almond oil is explained in the same way :—

$$\underset{\text{Bitter Almond Oil.}}{C_{28}H_{10}O_2.H_2} + O_2 = \underset{\text{Benzoic Acid.}}{C_{28}H_{10}O_2.O} + H_2O.$$

In order to be able to include the action of oxygen within his rule, he states the latter as follows :—When a compound is exposed to the dehydrogenising action of any substance, it takes up a quantity of this substance equivalent to the quantity of the hydrogen eliminated.

The doctrine of Dumas seems to me to be of most importance in this connection. He shows us that equal volumes of hydrogen, chlorine, bromine, and iodine are equivalent, while they possess only half the value of the same volume of oxygen. The difference between the two is clearly visible here, and this is the beginning of the separation of atom and equivalent.

The phenomena of substitution, or of metalepsy, as Dumas called it, were followed up further in the succeeding years by Dumas himself, as well as by Peligot,[35] Regnault,[36] Malaguti,[37] and, especially, Laurent ; and in particular, it is the independent extensions which the latter gave to Dumas' rule, that we shall now consider.

Laurent has enriched chemistry with a very large number of experimental investigations, but these, in many cases, are unfortunately wanting in the necessary accuracy. He had at his command only very limited resources, and instead of confining himself, on that account, to a few branches, Laurent, who was very fertile in ideas, preferred to start a great many things and to carry them out in a superficial manner. He destroyed, in this way, his reputation as an experimentalist, and was met with hostility at the very outset of his scientific activity ; while he was afterwards treated with unnecessary severity, especially by Berzelius and Liebig. This naturally reacted upon him, and he went his own way, and became gradually more incomprehensible, particularly in consequence of a nomenclature which was used almost exclusively by himself. Many of his clever and original ideas were thus lost to our science, or are now ascribed to the services of others. A great deal, on the other hand, was supplied to us first by Gerhardt, who was a friend and collaborator of Laurent for many years, and who combined a clear mode of expressing and of regarding chemical matters with probably more perspicuity and less genius.

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[35] Annalen. **12**, 24 ; **13**, 76 ; **14**, 50 ; **28**, 246. [36] Ibid. **17**, 157 ; **28**, 84 ; **33**, 310 ; **34**, 24, etc. [37] Ibid. **24**, 40 ; **25**, 272 ; **32**, 15 ; **56**, 268, etc.

At an early period, Laurent had begun to occupy his attention with the phenomena of substitution. He first studied naphthalene and its derivatives;[38] then, simultaneously with Regnault, the derivatives of ethylene chloride;[39] afterwards the action of chlorine upon compound ethers,[40] and upon the products of the distillation of tar, especially on phenol,[41] etc.

He very soon satisfied himself, by means of these various investigations, that the form which Dumas had given to the law of substitution was not a generally accurate one. He found that in very many instances there are more or fewer equivalents of chlorine or of oxygen taken up than there are of hydrogen eliminated, and *vice versa*; and that this is the case even with substances which do not contain oxygen, so that the exceptions cannot be explained by Dumas' second rule.[42] At the same time, however, Laurent points out that the substituted product, when it is produced by replacement of equivalent by equivalent, still exhibits certain analogies with the original substance; and he asserts that the chlorine introduced takes the place, and to a certain extent plays the part, of the hydrogen eliminated. His opinion may be stated somewhat in the following manner:—[43]

Many organic substances when treated with chlorine lose a certain number of hydrogen atoms, which escape as hydrochloric acid; chlorine atoms equal in number to the hydrogen atoms eliminated are substituted for the latter, so that the physical and chemical properties of the original substance are not essentially altered. The chlorine atoms thus occupy the space left vacant by the hydrogen atoms. In the new compound the chlorine to a certain extent plays the same part as the hydrogen did in the original substance.[44]

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[38] Annalen. **8**, 8; **19**, 38; **35**, 292; **41**, 98; **72**, 297; **76**, 298, etc.

[39] Ibid. **12**, 187; **18**, 165; **22**, 292.

[40] Ibid. **22**, 292.

[41] Ibid. **22**, 292; **23**, 60; **43**, 200, etc.

[42] See p. 141.

[43] Laurent, Méthode de Chimie. 242; E. 199; Thèse de docteur, Paris, 20 Dec. 1837, 11, 88, and 102; Ann. Chim. [2] **63**, 384; Comptes Rendus. **10**, 413; Revue Scientifique. **1**, 161.

Laurent endeavours to give expression to the observed facts and to the hypotheses based upon them, in the so-called nucleus theory.[45] This theory is of importance in our science (although it never obtained any general recognition in it) because we have adopted, even if in another form, many of the ideas embraced by it, and also because it was adopted by Gmelin as the basis of the organic portion of his excellent handbook. On this account I shall state the chief points of Laurent's doctrines.

According to Laurent, all organic substances contain certain nuclei, which he calls either fundamental (*radicaux fondamentaux*) or derived. The former are compounds of carbon with hydrogen, in which the mutual proportion of the number of the atoms is a simple one (1 to 2, 3, 4, etc., 2 to 3, etc.). For any definite proportion, several nuclei exist which are polymeric amongst themselves. Besides, these fundamental radicals are so chosen that the hydrogen and carbon atoms contained in them occur in pairs.

Subsidiary nuclei are formed from the fundamental nuclei by the substitution of other elements for the hydrogen; for example, chlorine, bromine, iodine, oxygen, nitrogen, etc. Laurent afterwards assumes replacement by radicals or groups of atoms. In such reactions Dumas' rule always holds, that the hydrogen turned out is replaced by equivalent quantities of other elements. But this is not the only kind of change that the nucleus can undergo, and here Laurent differs from Dumas. Thus an indefinite number of atoms may attach themselves to the radical, and be removed from it again without being replaced; whereas, as already stated, an atom cannot be removed from the nucleus without the entry of its equivalent, since the destruction of the whole group would otherwise ensue. Such destruction infallibly occurs as soon as carbon, in the form of carbonic anhydride, carbonic oxide, etc., is removed from the compound; in which case either a complete decomposition takes place, or a fresh nucleus is formed. The relation of this nucleus to the first one is not further defined, however. According to Laurent, the subsidiary nuclei show a great resemblance to the fundamental radicals in their physical and chemical characters; the derived nuclei, obtained by attachment of new atoms, have, on the other hand, acquired a different character. Thus a union with hydrogen and oxygen (water) usually brings about the formation of alcohol; a neutral oxide is formed by the taking up of two atoms of oxygen, a monobasic acid, by the taking up of four atoms, and a dibasic acid by the taking up of six atoms of oxygen.

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[44] I wish to recall the fact here, simply because a question of priority arose with respect to it (compare Comptes Rendus. **10**, 409 and 511), that Liebig and Wöhler, in their investigation of bitter almond oil, had already assumed that during the formation of benzoyl chloride the chlorine takes the place previously occupied by the hydrogen (compare p. 140). [45] Ann. Chim. [2] **61**, 125; compare also Gmelin, Handbuch. **4**, 16; **E. 7**, 18.

Laurent further adopts a geometrical conception respecting organic compounds. In accordance with this conception the nuclei are prisms in whose angles the carbon atoms are located, whilst the edges are formed by the hydrogen atoms. These edges can be taken away and replaced by others, without the figure undergoing any considerable changes. But should the place be left unoccupied, the internal connection would come to an end and the whole would fall to pieces. Atoms can still be added to the prisms so as to form pyramids; and the whole figure may be surrounded in this way, by which means its form is, of course, altered. These pyramids can be removed, whereupon the original prism makes its appearance again.

In our matter-of-fact science we are not accustomed to such imaginative views, and so it may appear as if nothing of any value for chemistry lies hidden behind them. In order to disprove this, however, I shall translate the hypotheses of

Laurent into our ordinary language. It will then be possible to obtain, moreover, a better grasp of Laurent's ideas.

The nucleus theory clearly sprang from the radical theory, but only by an essential reconstruction of the latter. The radical of Laurent is not an unalterable group of atoms, but it is a compound, which can be altered by substitution in equivalent proportions and does not lose thereby its characteristic properties. Thus Laurent is able to derive all his radicals from hydrocarbons, a proceeding which is, of course, in complete contradiction to the older ideas. These radicals can unite with other atoms, and in the substances so produced the nuclei are present as such; the nuclei pre-exist in the substances, and Laurent, therefore, entirely agrees on this point with his predecessors. By means of these two hypotheses, he is able to explain all the facts—not only the cases which follow Dumas' rule, but those also which are at variance with it, and of the latter he had found a large number. At the same time, his point of view furnishes reasons why both kinds of reactions are possible. On the assumption of the alterability of the radical, it may easily be understood that a group included far more compounds than was possible with the older radical theory. Laurent was thus able to discover far more of what we should now call "generic relationships," and that was an unquestionable advantage. Since he assumed the number of carbon atoms in the nucleus to be constant, substances were arranged into series according to the number of atoms of carbon they contained, and this supplied the basis of an excellent systematic classification. With him there was no connecting link between the series so formed; and in this respect Laurent's division differs from the classifications of the present day, which accentuate all relationships as much as possible. No such mode of treatment could, indeed, have been carried out at that time.

After these explanations, I may state that much that was new and good was advanced in Laurent's nucleus theory. Its importance lies principally in the fact that it was capable of a general application, and, as Gmelin proved, could be admirably employed as the basis of a detailed text-book. In this respect it is distinguished by very marked advantages over the radical theory, which, owing to the very definite form that had been given to the radical, could only be of service in certain directions, while it wholly overlooked various relationships.

I think it may be advantageous to show, by means of a few examples, the mode in which Laurent applied his theories, and also what his formulæ were for different compounds. In doing this I shall choose familiar groups of substances.

Nucleus, Etherene C_4H_8 $[C = 12]$[46]

Etherene Hydrochlorate	$C_4H_8 + H_2Cl_2$
Chloretherase	$C_4H_6Cl_2$
Chloretherase Hydrochlorate	$C_4H_6Cl_2 + H_2Cl_2$
Chloretherese	$C_4H_4Cl_4$ (then unknown)
Chloretherese Hydrochlorate	$C_4H_4Cl_4 + H_2Cl_2$
Chloretherise	$C_4H_2Cl_6$ (then unknown)
Chloretherise Hydrochlorate	$C_4H_2Cl_6 + H_2Cl_2$[47]
Chloretherose	C_4Cl_8
Etherose Chloride	$C_4Cl_8 + Cl_4$
Chloral	$C_4Cl_6O + H_2O$
Bromal	$C_4Br_6O + H_2O$
Chloracetic Acid (then unknown)	$C_4H_2Cl_4O + O_2$

Nucleus, Methylene C_2H_4

Chloroform	$C_2Cl_4 + H_2Cl_2$
Bromoform	$C_2Br_4 + H_2Br_2$
Cyanogen	C_2Az_2
Hydrocyanic Acid	$C_2Az_2 + H_2$
Cyanic Acid	$C_2Az_2 + O$[48]

Nucleus $C_{14}H_{14}$

Bitter Almond Oil	$C_{14}H_{10}O_2 + H_2$
Benzoic Acid	$C_{14}H_{10}O_2 + O$
Hydrobenzamide	$C_{14}H_{10}Az^{4}/_{3} + H_2$[49]

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[46] Ann. Chim. [2] 63, 388; Annalen. 22, 303.

[47] The principle of the nomenclature employed originated with Dumas (Ann. Chim. [2] 57, 305). Laurent almost always used this nomenclature.

[48] The symbol Az (Azote) was written for the nitrogen atom in France at that time (as it still frequently is). I have used it here for a reason that will be perceived further on.

[49] Ann. Chim. [2] 62, 23.

I have intentionally chosen these particular examples. They lead us to a point in Laurent's views which we have, up to the present, only very superficially touched upon. Since he assumed substitutions of hydrogen by nitrogen, we may inquire what the equivalent of nitrogen was. We recognise, from his deriving cyanogen from methylene, that Laurent assumed one atom (= 14 parts by weight) of nitrogen as equivalent to two atoms or parts by weight of hydrogen. This hypothesis did not accord with fact in the case of hydrobenzamide, which Laurent had obtained by treating bitter almond oil with ammonia. If the new substance was to be referred to the same nucleus as that from which he derived benzaldehyde, then two-thirds of an atom, or 9.33 parts by weight of nitrogen, must be equivalent to two parts by weight of hydrogen. Laurent did not know how to get out of this dilemma. The question was decided by Bineau.[50] In a detailed paper the latter endeavoured, in 1838, to give a solution to the problem of the determination of the equivalent of nitrogen. After a discussion of the fact that the common method of fixing this number is very arbitrary (considering that the quantity of a substance which, in its lowest stage of oxidation, unites with 100 parts by weight of oxygen is usually assumed to be equivalent to that quantity of oxygen, whereas it would be quite as justifiable to start from any other stage of oxidation), he adopts other considerations in respect to the matter. He obtains his evidence chiefly from the hydrogen compounds. He compares ammonia with water, and asks how many atoms of oxygen are necessary in order to oxidise completely the hydrogen united to one atom of nitrogen. It is known that 1½ atoms are required for this, consequently Bineau finds 14 parts by weight of nitrogen to be equivalent to 24 of oxygen and to 3 of hydrogen; in other words, the equivalent of the former, compared with 16 parts by weight of oxygen, is $9.33 = \mathrm{Az}\frac{2}{3}$. He introduces for nitrogen the symbol N, and points out that hydrobenzamide now accords with Dumas' rule. It can very easily be understood that Laurent accepted Bineau's determination.

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[50] Ann. Chim. [2] **67**, 225

On scarcely any side did the nucleus theory meet with acceptance. Dumas made use of much of it in advancing the theory of types, and although in doing so he mentions Laurent, still opinions which unquestionably were first stated by the latter, were ascribed to Dumas. No doubt, they met with acceptance earlier on account of the superior authority and position of Dumas.

Liebig, however, expressed himself very forcibly against Laurent,[51] and he was not altogether unjustified in his charges. In the application of his theory Laurent incurred blame for many arbitrary proceedings, which Liebig knew how to point out with much effect. Liebig further attacks the facts discovered by Laurent and employed by him in support of his opinions; and these are likewise not always able to withstand the keen criticism applied to them.

Much more violent still were the attacks of Berzelius,[52] which he erroneously directed against Dumas. The view that negative chlorine could take the place of positive hydrogen, without altering the nature of the product, was wholly inadmissible with the author of the electro-chemical theory. He makes every conceivable endeavour to bring the constantly increasing number of substitution products into harmony with his theories. I shall postpone, however, the detailed consideration of his views until a subsequent lecture, and shall close this one with an observation of Gerhardt's,[53] which enables us to recognise the clear and intelligent perception of this chemist, who at the time was still quite a young man.

Laurent's formula for Dutch oil was $C_4H_6Cl_2 + H_2Cl_2$. By treatment with chlorine this substance was said to be converted into chloride of carbon, C_4Cl_{12}.[54] According to Gerhardt, Laurent's formula is inaccurate because it assumes the decomposition of hydrochloric acid by means of chlorine, accompanied by the re-formation of hydrochloric acid.

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[51] Annalen. 25, 1. [52] Compare Comptes Rendus. 6, 629; and Berzelius' Jahresbericht 1840, 361. [53] J. pr. Chem. 15, 17. [54] Phil. Trans. 1821, 47.

LECTURE IX.

GRAHAM'S INVESTIGATION OF PHOSPHORIC ACID—LIEBIG'S THEORY OF POLYBASIC ACIDS, AND HIS VIEWS WITH RESPECT TO ACIDS IN GENERAL—ADOPTION OF THE DAVY-DULONG HYPOTHESIS—DISCOVERY OF TRICHLORACETIC ACID—ATTACK UPON THE ELECTRO-CHEMICAL THEORY—REPLIES OF BERZELIUS—COPULÆ.

I WISH to begin this lecture with some general remarks which may serve as an appendix to what was stated in the preceding lecture respecting the phenomena of substitution, and especially to the conceptions of them which were entertained by Dumas[1] and by Laurent.[2]

I desire to point out how, in consequence of the observed phenomena of substitution, the conception of the equivalent assumed a more definite form. Thus in assuming, with Dumas, that the quantities replacing one another are equivalent (and this was an assumption that had some justification, according to Laurent's views which rendered possible a direct comparison between the original and the final products), a series of experiments was all that was necessary in order to determine the equivalents of the substances so replacing one another. One section of chemists actually did work in this direction, and, in consequence of this, it is necessary to observe particularly to which school the author of any paper published at that time belongs; for at this very period Gmelin's school, which likewise wrote or desired to write in equivalent formulæ, began to acquire much influence. Whilst the adherents of the substitution theory (who made use of the equivalents), in spite of numerous shortcomings and mistakes, always endeavoured to separate from each other the conceptions of atom and equivalent, and to follow up both of them consistently, almost the opposite might be said of their opponents. The latter knew that one atom of alumina, Al_2O_3, requires three times as much sulphuric acid to saturate it as one atom of potash, KO; they also considered that one atom of phosphoric acid, P_2O_5, required three times (in reality twice) as much base to form a neutral salt as one atom of hydrochloric acid; and yet they did not hesitate to employ the name "equivalents" for these quantities.

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[1] Dumas, Traité, Organic Part, 1, 75.   [2] Annalen, 12, 187.

Just because our chemistry of to-day is based essentially upon the difference between the conceptions of atom and equivalent, everything that could lead to a distinction between these conceptions must be specially emphasised. I wished, therefore, to point out that a new means of determining equivalents was furnished, in the fourth decade of last century, by the phenomena of substitution, and that this involved a real advance in the question which is especially interesting us at present. But it was further shown, from an entirely different point of view, that the atoms of compound substances are not necessarily equivalent. Decisive reasons were advanced to establish the differences that exist, in this respect, in the case of the acids, which formed one of the most fully investigated classes of substances. The experiments relating to this matter were carried out at an earlier period than the advancement by Dumas of the theory of types, which was the next step in the development of the substitution theory, and on this account I think it should be treated of first. Even if both matters seemed at that time to be extremely diverse, still the exercise of some influence is not only conceivable, but it can actually be observed; and, for this reason, the chronological order must not be altogether lost sight of.

It is seldom that, in order to produce any great result, so few investigations have been necessary as was the case in the founding of the theory of polybasic acids. The experiment and the idea whereby this wide field of investigation was opened up to experimental science, while new and secure footing was afforded to theory, are alike elegant and precise.

Only a few persons took a part in this important crisis in chemistry, but they were valiant champions who conquered for us this domain. And, once set foot upon, the ground was secure, despite the contradiction of an authority whose words, although they had been observed in other cases in a scrupulously conscientious manner, were now spoken to the winds.

It is to Graham that the first impulse towards an alteration in the views regarding acids was due. Graham's investigation of phosphoric acid, and the way in which he states his results—the former free from preconceived notions and hypotheses, and the latter clear and definite—show us that we have to do with an acute and clear-minded thinker. When regard is paid to the ideas that were necessarily introduced as the direct result of the investigation, and when those intellectual advances are considered which were occasioned—not exclusively, it is true, but still to a great extent—by Graham's labours, it must be conceded that so much has seldom been accomplished by a single investigation.

As a consequence of Clark's investigation of phosphoric acid,[3] the view had been arrived at that this acid existed in two isomeric conditions, which, in their salts in particular, were stated to present great differences.[4] Common sodium phosphate gave a yellow precipitate with neutral silver salts, and the liquid possessed an acid reaction; the pyrophosphate, on the other hand, precipitated white silver pyrophosphate and the neutrality remained. It was known, of course, that the one sodium salt crystallised with more water than the other, but this was regarded as water of crystallisation, and no importance was attached to it; so that the two acids were looked upon as isomeric modifications.[5] Graham rectified this mistake. He succeeded in throwing light upon this hitherto obscure subject by proving that the water which was contained in the hydrated acids should not be disregarded as inessential to their constitution, but that, on the contrary, it assumed the function of the base.[6] Graham showed, in 1833, how ordinary phosphoric acid and all its salts may be regarded as compounds of one atom of phosphoric acid, P_2O_5, and three atoms of base which can be completely or partially replaced by water. Thus, according to him, ordinary (neutral) sodium phosphate consists of one atom of phosphoric acid combined with two atoms of soda and one of water: on mixing its solution with silver nitrate, the silver salt with three atoms of silver is precipitated, whilst sodium nitrate and nitric acid remain in the solution together. Exceptions to Richter's law (already observed in similar cases by Berthollet), where the mixture becomes acid when the solutions of two neutral salts are mixed,[7] were thus explained. In this case two atoms of soda and one of water were exchanged for three atoms of silver oxide.

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[3] Edinburgh Journal of Science. 7, 298; Schweigger's Journal. 57, 421.

[4] See also Stromeyer, Schweigger's Journal. 58, 123.

[5] Compare Berzelius, Lehrbuch, Third Edition, 2, 60.

Another very important result of Graham's investigation is met with in the analysis of pyrophosphoric acid and its compounds. Graham shows that on heating the sodium salt mentioned above to over 350°, the water it contains is driven off, and that sodium pyrophosphate, identical with the salt already known, is produced in this way. This salt is not, however, isomeric with the original one, as had been supposed, but differs from it by containing one atom of water less; and this is of essential importance in regard to the nature of the acid. The white precipitate, too, which is produced by silver salts, only contains two atoms of silver oxide; and it is thus a quite general property of pyrophosphoric acid to saturate only two atoms of base (or of water), which distinguishes it very sharply from ordinary phosphoric acid. In the latter the ratio of the oxygen in the base to that in the acid is as 3 to 5; in the other acid it is as 2 to 5.

Graham finds further that on heating the acid sodium phosphate, which consists, according to him, of one atom of phosphoric acid, one atom of soda, and two atoms of water

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[6] Phil. Trans. 1833, 253; A.C.R. No. 10; Annalen. **12**, 1.

[7] Berthollet, Stat, Chim, **1**, 117; E. **1**, 85.

(as base), both water atoms are driven off, and a hitherto unknown salt, sodium metaphosphate, is produced. The acid contained in this salt is characterised by being saturated by one atom of base, whilst, in the free state, it contains one atom of water. The silver compound was again different from either of the others. In this case the ratio of the quantities of oxygen in base and acid was as 1 to 5.

Finally, it was shown in the investigation that meta- and pyro-phosphoric acids, as well as the majority of their salts, pass into ordinary phosphoric acid or a salt derived from it, when boiled with water, or still better, when fused with sodium carbonate.

Two important theoretical conclusions can be directly deduced from Graham's investigation.

(1.) In acids there is a certain number of atoms of water, and salts are formed by the replacement of these.

(2.) The atoms of the acids are not always equal in number to the atoms of the bases, and in some, even the ratio is variable. Thus Graham showed how, from the same phosphoric anhydride, to prepare three hydrates which were able to take up quite different quantities of base.

Liebig, in 1838, stated these conclusions with great clearness and precision.[8] A man of his genius could not, however, rest satisfied with publishing thoughts that were merely conclusions drawn from the experiments of others. We are indebted to Liebig for an excellent investigation of a series of organic acids, from which it appeared that phosphoric acid does not stand alone with respect to its behaviour towards bases, but that in the cases of certain other acids, one atom likewise possesses the property of saturating several atoms of base. Founding, as he did, upon a broader basis, he was then able to introduce the idea of the polybasic acids.

Liebig's experimental investigation embraces fulminic, cyanic, meconic, comenic, tartaric, malic, citric, and other acids. He finds relations amongst the salts of each of these acids, which are similar to those in the case of phosphoric acid. But he endeavours, especially, to range the three cyanogen acids, *i.e.*, cyanic, fulminic,[9] and cyanuric, side by side with the three phosphoric acids. In the former, as well as in the latter, there is present, according to him, a group of atoms which has the power of saturating sometimes one, sometimes two, sometimes three atoms of base. But whilst the atomic weight is not altered in the case of the phosphoric acids, it increases in that of the cyanogen acids in the same ratio as the saturating capacity, so that the resulting salts are polymeric with one another. In the latter case, the quotient obtained by dividing the quantity of oxygen in the acid by that in the base, remains unchanged, whereas this, according to Graham, is not the case with the varieties of phosphoric acid.

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[8] Annalen. **26**, 113; compare Comptes Rendus. **5**, 863.

Liebig writes:

$3MO.P_2O_5$	Phosphate.	$3MO\ Cy_6O_3$	Cyanurate.
$2MO.P_2O_5$	Pyrophosphate.	$2MO\ Cy_4O_2$	Fulminate.
$MO.P_2O_5$	Metaphosphate.	$MO\ Cy_2O$	Cyanate.

Of distinctly greater importance are the considerations which lead Liebig to propose a separation, from the other acids, of those which behave in a way analogous to phosphoric acid. The course of his argument in this matter is approximately as follows: The relations are not so complicated in the cases of all the acids which share with phosphoric acid the characteristic property of neutralising several atoms of base by one atom of acid, as they are in the case of phosphoric acid itself; and hence it is not so easy to establish in all cases that they belong to this category. In the case of phosphoric acid, no matter what number may be chosen as its atomic weight, it can never be shown that one atom of acid saturates one atom of base in all three modifications.[10] What, now, are the characteristics that enable us to recognise that we have to do with a substance belonging to this group?

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[9] Liebig assigns to fulminic acid the formula $2H_2O.Cy_4O_2$ [H=1, C=12, O=16].

[10] Here, as in the foregoing, the word acid is to be understood as referring to the anhydride.

Liebig has recourse to experiment in order to decide this highly important question. He compares the behaviour of phosphoric acid with that of sulphuric acid, a compound concerning which he has no reason for reckoning it in this class. In doing so he says :—[11]

"If to acid sulphate of potash, we add another base which is not isomeric with potash and which forms with sulphuric acid a salt free from water of halhydration,[12] soda for example, the acid salt separates into two neutral ones, Glauber's salt and sulphate of potash, which crystallise apart from each other.

"If, on the other hand, a certain quantity of potash is added to acid phosphate of soda, phosphate of soda and potash is formed, wholly analogous in its composition to the acid salt. It contains three atoms of base ; two of these are soda and potash ; one of the two atoms of water previously contained in it, is replaced by potash, the second atom remains in the composition of the new salt.

"This behaviour distinguishes phosphoric acid and arsenic acid from the great majority of all other acids: their power of forming salts of the same class with different bases, differing from those which are called double salts, depends essentially upon their property of combining with several atoms of base. *I regard this character as decisive respecting the constitution of these, and of all acids which form compounds similar to those of phosphoric acid.*"

A criterion is thus found for separating phosphoric acid and its analogues from the other acids, and Liebig employs it in order to establish the fact that all the substances examined by him belong to this class. The grounds upon which he also decides to include tartaric acid in this group are very interesting and important. This acid was at that time written $C_4H_4O_5$, so that its atom saturated only one atom of base. The existence of Rochelle salt and of tartrate of potash and ammonia, which can be obtained from the acid potassium compound by neutralising with the corresponding bases, proves to Liebig that tartaric acid also possesses the property of neutralising two atoms of base; and this leads him to double its atomic weight, *i.e.*, to write it $C_8H_8O_{10}$. The talented author of this famous paper thus understood very well that the considerations here advanced furnish a new aid to the determination of the atomic weight.

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[11] Annalen, **26**, 144-145. [12] Liebig regards as water of halhydration, that water in salts which can be separated and replaced by equivalents of neutral salts.

Liebig justifies the separation of the acids into different groups, in the following words:—[13]

"The acids might be divided into *monobasic*, *dibasic*, and *tribasic*. By a dibasic acid there would be understood one whose atoms unite with two atoms of base in such a way that these two atoms of base replace two atoms of water in the acid. The conception of a basic *salt* thereby remains unchanged. . . . Accordingly, when two and more than two atoms of base combine with one atom of an acid, and only one atom of water is separated during the operation (fewer therefore than the number of equivalents of the fixed base), then a really basic salt is produced." . . .[14]

This great step was thus taken. The way had been prepared for it by the labours of Graham; the change was carried through and established by Liebig's investigations. If we desire to be strictly just (and we set some value upon this), we must not suppress the fact that Liebig published the first paper on this subject along with Dumas in 1837.[15] This was the only fruit of the proposed association of these two chemists.

In the same paper in which Liebig develops, in detail, the theory of the polybasic acids (in accordance with which the acids fall into several classes), he endeavours, by means of a

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[13] Annalen. **26**, 169.

[14] In the property of forming pyro-acids Liebig also finds a ground for classing acids as polybasic (*loc. cit.* 169).

[15] Comptes Rendus. **5**, 863. According to a letter which Liebig addressed to the French Academy in 1838 (Comptes Rendus. **6**, 823; Annalen. **44**, 57), it appears that the share of Dumas in this investigation was very unimportant.

"hypothesis," to get rid of the division, which had subsisted up to this time, into hydrogen acids and oxygen acids. This hypothesis is a reversion to the ideas of Davy and of Dulong.[16]

A similar attempt had previously been made by Clark, although much less elaborated. According to Griffin,[17] Clark stated views of this kind in his lectures as early as 1826. As he himself wrote to Mitscherlich in 1836,[18] he finds grounds for his opinion in the isomorphism of sulphate of soda and permanganate of baryta. At that time, the formulæ assigned to these compounds were:

$$NaOSO_3 \text{ and } BaOMn_2O_7,$$

according to which they contained an unequal number of atoms. Clark proposes to double the atomic weight of sodium (that is, to assume it to be four times as great as at present) and to assign to it the number that Berzelius adopted in 1819.[19] Since he further regards the acids as hydrogen compounds, from which salts are produced by the replacement of the hydrogen by metals, sulphuric acid, with him, is H_2SO_4 and permanganic acid $HMnO_4$; and therefore sulphate of soda is NaS_2O_8, and permanganate of baryta is $BaMn_2O_8$; and by this means he attains similarity in the number of atoms in both compounds.

Quite different grounds, which are of much superior value, and are more numerous, lead Liebig to revive again the Davy-Dulong hypothesis. Graham had shown that pyro- and meta-phosphoric acids can exist in aqueous solution without at once passing into ordinary (tribasic) phosphoric acid. Liebig consequently inquires whether these three acids really differ from one another by an atom of water in each case, and whether it is the gain or loss of water which brings about the changes in the basicity of phosphoric acid. He does not believe that convincing grounds can be found for the adoption of this hypothesis; so that the contrary supposition, in accordance with which the salts are formed by the replacement by metals of the hydrogen of the (hydrated) acid, is not to be rejected unconditionally. The accuracy of this idea being premised, the acids would not contain any ready-formed water, and they could not be any longer regarded as consisting of anhydride and water, any more than the salts were compounds composed of acid (anhydride) and base.

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[16] Compare p. 83.

[17] Griffin, The Radical Theory in Chemistry, London (1858), 4 *et seq.*

[18] Annalen. **27**, 160.

[19] Compare p. 94.

Liebig finds an important support for the latter hypothesis (in accordance with which the metals, as such, should be assumed in salts) in the behaviour of tartar emetic at a high temperature. According to the analysis, the formula $C_8H_8KSb_2O_{14}$ represents the compound dried at 100°. It was assumed to contain an atom of anhydrous tartaric acid, an atom of potash, and an atom of oxide of antimony, so that its formula was written $C_8H_8O_{10} + KO + Sb_2O_3$ (assuming that the formula of tartaric acid was doubled). According to Liebig this substance, on being heated to 300°, loses two more atoms of water, a property which it does not share with any other salt of the same acid. The assumption of the presence of water in the acid, hitherto regarded as anhydrous, appears objectionable to Liebig on account of the consequences which would follow from it, and so he believes that nothing remains but to ascribe the formation of water to the reduction of the oxide of antimony. The actual existence of a base, in the metallic condition, combined with an oxygen acid (even if only for certain compounds) would no longer require to be regarded as a mere supposition.[20]

On another occasion, when discussing these relations, Liebig writes the formula for tartaric acid, $C_8H_4O_{12}.H_8$, and that of tartar emetic which has been heated to 300°, $C_8H_4O_{12}\begin{cases}K\\Sb_2\end{cases}$, and I must not omit to draw attention to the fact that the displacement of three atoms of hydrogen by one atom of antimony, is here assumed.[21]

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[20] Annalen. **26**, 159.

[21] The paper in question is by Dumas and Liebig, Comptes Rendus, **5**, 863.

Liebig admits that it is difficult to understand how potash is reduced by means of sulphuric acid, an assumption which must be made in case sulphate of potash is to be regarded as a potassium compound; but he instances a case in which a hypothesis of the kind is indispensable to the explanation of the facts. The decomposition of thiocyanate of silver by means of sulphuretted hydrogen, with the formation of sulphide of silver and free acid, would be contrary to all views regarding affinity if the salt corresponded to the formula $AgS + Cy_2S$; whereas the reaction becomes a normal one, assuming the formula to be $Ag.Cy_2S_2$. Unsatisfactory as it is at first sight, the hypothesis of the reduction of the oxides by means of acids, further gives an explanation of the behaviour of many acids which exhibit a higher capacity for saturation towards silver oxide than they do towards soda, although the latter is endowed with more strongly basic properties.

Finally, Liebig points out that by the assumption of the hypothesis of Dulong, the grouping of the hydrogen acids and of the oxygen acids into one class, which is almost enforced by the similarities in their reactions, is attained. Thus lime always gives up the same quantity of water no matter whether it is neutralised with sulphuric acid or with hydrochloric acid. The mode of explanation then adopted, in accordance with which the water, in the one case, was present in the acid ready-formed, and in the other case was produced during the action, according to Liebig takes no account of the analogy of the two cases. He tries to pull down the barrier, and his words are sufficiently significant to deserve a place here.[22]

"We employ, therefore, two modes of explanation for one and the same phenomenon; we are forced to ascribe to water the most varied properties; we have basic water, water of halhydration, water of crystallisation; we observe its entrance into compounds in which it ceases to assume any one of these three forms; and all this is for no other reason than that we have drawn a distinction between haloid salts and oxygen salts, which we do not observe in the compounds themselves; in all their relations they possess properties of the same kind."

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[22] Annalen. **26**, 179.

Liebig then returns to Davy's ideas, and in doing so he states his views as follows:—[23]

"*Acids* are, accordingly, certain compounds of hydrogen, in which the hydrogen can be replaced by metals.

"Neutral *salts* are those compounds of the same class, in which the hydrogen is replaced by the equivalent of a metal. Those substances which we at present call anhydrous acids, acquire the property of forming salts with metallic oxides, for the most part, only on the addition of water; or they are compounds which decompose the oxides at a high temperature.

"On bringing together an acid and a metallic oxide, the hydrogen is separated, in the majority of cases, in the form of water. It is a matter of complete indifference for the constitution of the new compound, in what manner the formation of this water is conceived: in many cases it is formed by the reduction of the oxide; in others it may be produced at the expense of the elements of the acid—we do not know which.

"We only know that, without water, no salt can be produced at ordinary temperatures, and that the constitution of the salts is analogous to that of the hydrogen compounds which we call acids. The principle of the theory of Davy, which must be kept especially in sight in criticising the theory, is that he makes the capacity of saturation of an acid dependent upon the hydrogen or upon a part of the hydrogen which it contains; so that, if the other elements of the acid, collectively, are called the radical, the composition of the radical does not possess the most remote influence upon this capacity."

These statements are recognised, on the whole, as correct even at present. Together with what I have stated above concerning the polybasic acids, they constitute the basis of our views regarding acids. No doubt the characters which distinguish polybasic from monobasic acids were considerably extended by Gerhardt and Laurent, so that the conceptions and definitions assumed a much more fixed and decided form. The distinction between the basicity and the atomicity of an acid was learned at a still later date, and rules were formulated whereby these also can be ascertained numerically. But these developments fall into a period which is too far removed from the one now under consideration for us to be able to discuss them here at present.

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[23] Annalen. **26**, 181.

It will easily be understood that Berzelius could not share Liebig's opinions. To recognise them would have been to abandon dualism, the basis of his own theories. It is true that the new way of looking at substances was not purely unitary; the acids were supposed to consist of radical and hydrogen, and the salts, of radical and metal, so that there still existed a division into two parts; but this was in a sense in which Berzelius could not admit it. The mode of salt formation, as Liebig conceived it, must especially have been in opposition to his views. There were no longer two compounds of the first order—an electro-positive and an electro-negative constituent—which united; the formation of salts consisted, instead, in the replacement of hydrogen. How could this be reconciled with the electro-chemical theory, in accordance with which compounds are only formed by the union of atoms one with another? Hence we find Berzelius also protesting[24] against the theory of hydrogen acids, if I may thus designate Dulong's ideas. His reasons were not sufficient, however, to dissuade the greater number of chemists from adopting this theory, and on this account I shall not enter more minutely into the matter, but shall again turn to the facts which were to lead to a unitary system. I refer to the phenomena of substitution, or to the replaceability of hydrogen by electro-negative elements.

Besides Dumas and Laurent, Regnault and Malaguti were especially engaged in the investigation of this subject. The results obtained by these chemists—the theories of Laurent, as well as Liebig's views concerning acids—had not been without influence upon Dumas. An extremely interesting discovery, which he makes in 1839, obliges him to expound his views at this time with respect to substitution; and also to retract, partially at least, the statements previously advanced and to introduce in their place new ones of far greater significance. In this way, from the empirical rules of substitution, the theory of types arises.

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[24] Berzelius, Jahresbericht 1839, 264; Annalen. 31, 1.

By the action of chlorine, in sunlight, upon acetic acid, Dumas had obtained a crystalline substance whose composition could be expressed by the formula $C_4Cl_6H_2O_4$,[25] and which could, therefore, be regarded as acetic acid, $C_4H_8O_4$, in which six atoms or volumes of hydrogen were replaced by six atoms of chlorine.[26] The interesting and important part of this reaction lay in the properties of the new compound, which Dumas called chloracetic acid. This acid had the same saturating capacity as acetic acid, so that Dumas was able to assert that by the entrance of chlorine in place of the hydrogen, the chief character of the compound was not altered; or, as he expresses himself, "that in organic chemistry there are certain types, which persist even when an equal volume of chlorine, bromine, or iodine is introduced into them in place of the hydrogen which they contain.

It will thus be seen how Dumas, in consequence of his discovery of chloracetic acid, is led to the same point of view which had already been taken up by Laurent, but which the former had at first put aside as extending beyond the limits of fact.[27] It is, however, an injustice to Dumas to represent his theory of types as merely an application or perhaps an expansion of Laurent's ideas. Laurent was a clever speculative thinker; but he did not hesitate to state a hypothesis for which a complete scientific proof could not, at the time, be adduced, and this, I think, was the case with respect to his views concerning substitution. That this, at least, was the impression made upon his contemporaries is to be seen from

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[25] In the French papers Dumas retains the atomic weight C=6.
[26] Annalen. 32, 101. [27] Comptes Rendus. 6, 689. At that period Dumas called Laurent's theory an extension of his ideas which did not concern him.

Liebig's criticism of Laurent's theories.[28] The facts were still wanting, which showed, in a definite and decisive manner, the analogy between the original substance and the final product. Our science cannot advance by means of ideas alone: it is only when an opinion is called forth, and to a certain extent necessitated, by experiment that a further development is involved in it. It was not Dumas' position and name alone that now procured favour for the theory which, a year before, had scarcely been taken notice of. The chemists of that period had no such respect for authority. The discovery of chloracetic acid lies between the promulgation of the nucleus theory and that of the theory of types; and even if "a theory can be made up of words" still, in chemistry, greater value is, fortunately, placed upon a decisive experiment than upon daring speculations.

An analogy between acetic and chloracetic acids could not remain unobserved; and especially after Berzelius, who had his reasons for not admitting any similarity between them, had given prominence to their differences, and, with a certain amount of irony, inquired for their kindred relationships.[29] Dumas shows the reactions which they undergo by the influence of potash, and points out their similarity.[30]

We have—

$$C_4H_2Cl_6O_4 = C_2O_4 + C_2H_2Cl_6$$
$$C_4H_2H_6O_4 = C_2O_4 + C_2H_2H_6.$$[31]

Besides carbonate of potash, there is formed, in the one case, marsh gas, and in the other, chloroform; *i.e.*, two substances which again exhibit the same difference in composition, the one from the other, as the two acetic acids do; and of which the latter, as Dumas also particularly shows,[32] can be obtained from the other by the action of chlorine.

By the discovery of trichloracetic acid a basis is furnished upon which Dumas erects his theory of types.[33] Thus, according to him, all substances which contain the same number of equivalents combined in the same way, and of which the chief characters are similar, belong to the same chemical type. These are, for the most part, compounds which can be obtained from one another by very simple reactions, such as acetic acid and chloracetic acid; chloroform, bromoform, and iodoform; ethylene and the products arising from it by substitution by means of chlorine.

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[28] Annalen. 25, 1.

[29] Berzelius, Jahresbericht 1840, 367 etc.

[30] Annalen. 33, 179.

[31] This latter reaction appears to have been discovered previously by Persoz (Introduction à l'Etude de la Chimie moléculaire), as was pointed out by Pelouze and Millon (Annalen. 33, 182).

[32] Annalen. 33, 187 and 275.

Dumas thinks he has found, in the conception of the chemical type, the basis of a new classification, which includes the recently observed facts; but he employs, at the same time, the molecular type introduced by Regnault,[34] which he calls also the mechanical type. To this type the following compounds belong:—

Marsh gas	$C_2H_2H_6$
Methyl ether	$C_2O\ H_6$
Formic acid	$C_2H_2O_3$
Chloroform	$C_2H_2Cl_6$
Chloride of methyl	$C_2Cl_2H_6$
Chloride of carbon	$C_2Cl_2Cl_6$

These substances, which may be regarded as arising by substitution from one another, and which may possess very different properties, are classed in one natural family. The point of view which led to the establishment of Regnault's types, is a much more comprehensive one than that from which Dumas was induced to advance his chemical types, the substances embraced under the latter heading constituting merely a subdivision of those which must be classed under the same mechanical type. Dumas also sees this clearly, for he says:[35] "On every occasion when a substance undergoes change without quitting its molecular type, it is changed in accordance with the law of substitution. On every occasion when a substance passes, on undergoing modification, into another molecular type, the law of substitution is no longer adhered to during the reaction." And further: "Alcohol, acetic acid, and chloracetic acid belong to the same natural family; acetic acid and chloracetic acid to the same species." It may therefore be said that, so far as the idea goes, mechanical type and nucleus amount to the same thing; both comprise the substances which arise from one another, or which can, at least, be looked upon as arising from one another, by equivalent substitution.

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[33] Annalen. 33, 259; 35, 129 and 281; 44, 66.

[34] Ibid. 34, 45.

[35] Ibid. 33, 279.

Dumas, as may have been observed, has now arrived at the opinion that his law of substitution is not applicable to all reactions, and that an equivalent of another element is not always taken up even for the hydrogen removed. He is all the more obliged to admit this, since he now no longer assumes the existence of ready formed water in organic substances (alcohol, for example[36]) whereby his second rule ceases to hold.[37] He is obliged, in consequence, to recognise, and he does it explicitly, that the phenomenon of substitution is not a general one; he even finds in this one of its most essential features.[38]

While he thus limits the applicability of the law of substitution, the validity of the law in another direction is enhanced. According to Dumas, it is not only the hydrogen of an organic substance that can be replaced, but all the elements which it contains. True substitution of the oxygen, of the nitrogen, and even of the carbon may be accomplished;[39] and these elements may be replaced, not only by others, but also by compound groups such as cyanogen, carbonic oxide, sulphurous acid, nitric oxide, nitrous acid, amide, etc. The assumption of the replaceability of carbon, which at that time met with the most vigorous contradiction as a silly hypothesis, and was, in Germany, made the subject even of ridicule,[40] was a consequence of the experiments of Walter[41] who had obtained sulpho-camphoric acid by the treatment of camphoric acid with sulphuric anhydride, carbonic oxide being evolved. Dumas regarded this acid as camphoric acid in which one atom of carbon was replaced by the group SO_2.

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[36] Annalen. 33, 261. [37] Compare p. 141. [38] Annalen. 33, 264. [39] Ibid. 33, 269. [40] Ibid. 33, 308. [41] Ibid. 36, 59.

If the conception of the molecular type is regarded in its widest sense, it may be said that this idea of Dumas as to the replacement of carbon, was wholly justified by subsequent experiments. Wöhler has pointed out a substitution of carbon by silicon;[42] and by means of reactions quite analogous to those employed for converting a hydrocarbon into the corresponding alcohol, Friedel and Crafts have transformed ethyl silicide into silico-nonyl alcohol which, as the name indicates, they look upon as nonyl alcohol in which one atom of carbon is replaced by one atom of silicon.[43] More recently, silicon compounds have been discovered which are not only to be regarded as analogous to certain carbon compounds, but which behave in a manner similar to the latter. This is particularly the case with triethyl silicol.[44]

I may also remark here that the view of Dumas concerning the replacement of carbon was in contradiction to the nucleus theory of Laurent, and rendered difficult the classification of organic substances according to the number of their carbon atoms. The ideas of the two chemists approach each other more closely as regards the conception of the radical than as regards its composition. Dumas now expressly states also that the radical is not an unalterable group, but that in it, just as in all compounds, the atoms are replaceable by others. Gerhardt had, however, advanced similar views two years earlier, and we shall, therefore, have to deal fully with this point afterwards in another lecture.

The first, and probably the most important consequence of the theory of types was that it demanded a unitary mode of regarding substances. The compound was no longer to be regarded as consisting of two parts. It constituted, rather, a uniform whole, which might undergo change from the fact that one atom could take the place of another. Dumas compares it with a planetary system ; the atoms here represent the individual planets, and they are held together by affinity instead of by gravitation. The atoms in this system can be replaced by others: so long as the number of the equivalents and the relative positions of the atoms are preserved, the system is unchanged.

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[42] Annalen. **127**, 268. [43] Comptes Rendus. **61**, 792; also Annalen. **138**, 19; compare further Friedel and Ladenburg, Annalen. **143**, 118; **145**, 174 and 179; **147**, 355; and Comptes Rendus. **66**, 816. [44] Ladenburg, Annalen. **164**, 300.

According to the theory of types, the properties of a compound were affected far more by the arrangement than by the nature of the atoms ; and this doctrine which Dumas now defends as confirmed by experiment, leads him to an attack upon the electro-chemical theory. This is how he expresses himself :—[45]

"One of the most immediate consequences of the electro-chemical theory is the necessity of considering all chemical compounds as binary substances. It is necessary to find out, in every one of them, the positive and the negative constituents, or the groups of particles to which these two distinctive characters are ascribed. No view was ever more fitted to retard the progress of organic chemistry." And in another place : [46] "In general, when the substitution theory and the theory of types assume similar molecules, in which some of the elements can be replaced by means of others without the edifice becoming modified either in form or outward behaviour, the electro-chemical theory splits these same molecules, simply and solely, one may say, in order to find in them two opposite groups, which it then supposes to be combined with each other in virtue of their mutual electrical activity."

Dumas does not deny the influence of electrical forces upon chemical reactions. On the contrary, chemical and electrical forces might, according to him, even be identical. What he attacks is the electro-chemical theory of Berzelius, in accordance with which hydrogen is supposed to be always positive, and chlorine always negative. He believes that in the formation or decomposition of compounds he can recognise the action of electrical forces; but what he declares to be erroneous, and irreconcilable with the phenomena of substitution, is the assumption that the electrical state of the atoms is unchanging.

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[45] Annalen. 33, 291. [46] Ibid. 33, 294.

The fatal moment had now arrived; it was a question of defending dualism, and also the electro-chemical theory, which was in the fullest agreement with it and had prevailed, almost unattacked, for nearly twenty years, against the views that had been stated in opposition to it. Ways and means had to be devised whereby the newly-discovered facts with respect to substitution could be brought into harmony with the electro-chemical ideas.

Before the storm actually broke, Berzelius had perceived the threatening clouds gathering about him and had taken his precautions. As soon as Laurent had assumed, in his first papers, that the hydrogen of the nucleus (or fundamental radical) could be replaced by chlorine, Berzelius, quite correctly perceiving the danger to his theories which such views might possess, energetically repudiated the statements of Laurent.[47] The entrance of electro-negative elements into radicals is put aside as an untenable hypothesis; and even the oxygen radicals, which he had greeted with so much pleasure a few years previously, are discarded. This assumption is, according to Berzelius, "of the same kind as that which would regard sulphurous acid as the radical of sulphuric acid, and manganese peroxide as the radical of manganic acid. An oxide cannot be a radical. The conception of the word radical is such that it represents the substance which, in an oxide, is combined with oxygen."

Berzelius now only recognises radicals which contain carbon and nitrogen, carbon and hydrogen, or carbon, nitrogen, and hydrogen.

Sulphur "cannot enter into the composition of a radical any more than oxygen can." "The ternary radicals" must therefore be regarded "either as compounds of a binary substance with a simple one, or as compounds of two binary substances."[48]

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[47] Berzelius, Jahresbericht 1839, 358.

The radical $C_{14}H_{10}$ is now constituted the basis of the compounds discovered by Liebig and Wöhler, and this is justified by the analogy which benzoic acid, benzoyl, and the hydrocarbon $C_{14}H_{10}$ exhibit with manganic acid, manganese peroxide, and manganese. Thus:

$C_{14}H_{10}O_3$	Benzoic acid -	MnO_3	Manganic acid.
$C_{14}H_{10}O_2$	Benzoyl - -	MnO_2	Manganese peroxide.
$C_{14}H_{10}$	- - - -	Mn	Manganese.[49]

Berzelius regards benzoyl chloride as similar to chromyl chloride, adopting for the latter the formula of H. Rose.[50] He writes:

$2CrO_3 + CrCl_6$ - - - Chromyl chloride.
$2C_{14}H_{10}O_3 + C_{14}H_{10}Cl_6$ - Benzoyl chloride.

Quite analogous with this is the formula of phosgene, which substance Dumas regarded as carbonic acid in which one atom of oxygen is replaced by two atoms of chlorine.[51]

Berzelius writes $CO_2 + CCl_4$, Phosgene.

At this time Berzelius is putting dualism more prominently forward than ever, and in his view these formulæ are entirely justified. "Since, in accordance with our present views, the forces which bring about chemical combinations do not act between more than two substances of opposite electro-chemical tendencies, all compound substances must permit of being split into two constituents, of which the one is electro-positive and the other electro-negative."[52]

In consequence of these views, all substances which, besides carbon and hydrogen, also contain oxygen, chlorine, bromine, or sulphur, break up into several parts which often appear to be chosen quite arbitrarily; further the atomic weight is frequently doubled or trebled, so that the subdivision into binary radicals may be carried out. Highly complicated formulæ are thus obtained, of which I can only instance a few:

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[48] Annalen, **31**, 13. [49] Compare also Berzelius, Lehrbuch. Third Edition, **6**, 205. [50] Pogg. Ann, **27**, 573. [51] Dumas, Traité, **1**, 400. [52] Annalen, **31**, 12.

Malaguti's chlorinated ether:

$$C_4H_6O_3 + 2C_4H_6Cl_6.$$[53]

Malaguti's chlorosulphuretted ether:

$$(C_4H_6O_3 + 2C_4H_6Cl_6) + (C_4H_6O_3 + 2C_4H_6S_3) \text{ etc.}$$[54]

His conception of chloracetic acid is very important as we shall find further on; he regards it as a compound of oxalic acid with chloride of carbon:

$$C_2Cl_3 + C_2O_3$$

whilst acetic acid remains as the trioxide of the radical acetyl, C_4H_6 or $C_4\text{Ħ}_3$. Even in 1840 he still disputes the similarity in the constitution of the two compounds, and does not permit himself to be shaken in this by their analogous behaviour with potassium hydroxide.[55]

This view was not long tenable, however, in face of the constantly increasing number of substitution products, very many of which exhibited unmistakable analogies with the original substances. When Melsens succeeded, in 1842, in reconverting chloracetic acid into acetic acid, by treatment with potassium amalgam,[56] and thus proved that chlorine can be replaced by hydrogen again so that the original substance is reproduced, even Berzelius was compelled to make an admission. He says[57]—"If we recall to memory the decomposition of acetic acid by means of chlorine with formation of *Chlorkohlenoxalsäure* (chloracetic acid), another view as to the composition of acetic acid presents itself as possible. In accordance with this view it would be a coupled[58] oxalic acid whose copula is C_2H_3, as the copula of the *Chlorkohlenoxalsäure* is C_2Cl_3; consequently the action of chlorine upon acetic acid would consist in the conversion of the copula C_2H_3 into C_2Cl_3."

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[53] Berzelius, Jahresbericht 1840, 375; here also Berzelius still writes Ħ instead of H_2.

[54] Annalen. **31**, 113; **32**, 72.

[55] Ibid. **36**, 233.

[56] Ann. Chim. [3] **10**, 233.

[57] Lehrbuch. Fifth Edition, **1**, 460 and 709.

[58] Berzelius here employs a word that had been introduced into the science by Gerhardt.

Perhaps Berzelius did not notice that he had thus conceded the chief point in the theory of substitution which, a few years before, he had vigorously contested. Chlorine could replace the hydrogen of the "copula," and the constitution of the compound was not essentially altered thereby. Berzelius now wrote:

$C_2O_3 + C_2Cl_3$ Chloracetic acid.
$C_2O_3 + C_2H_3$ Acetic acid.

Was not a fundamental principle of the electro-chemical theory violated by this concession? I think it was. It was now necessary to assume either that forces different from the electrical forces are present in the copula, or that the electrical properties of the elements are altered in the compound; and both of these assumptions were much at variance with the former ideas of Berzelius.

The substitution theory had thus come off victorious. Berzelius, it is true, never admitted his defeat, but, as a matter of fact, he had given in. The electro-chemical theory was now abandoned. In its last throes it had produced the idea of copulæ: had these latter any vitality? At first it did not seem so; they were looked upon as the idle invention of a wearied intellect. With this I partly agree; but they still possessed a spark of life, otherwise they would not have been capable of development, and it would not have been possible even for a man like Kolbe to advance them to what they afterwards became.

This subject will be dealt with in a subsequent lecture.

LECTURE X.

INFLUENCE OF THE SCHOOL OF GMELIN—THEORY OF RESIDUES—COUPLED COMPOUNDS—GERHARDT'S DETERMINATION OF EQUIVALENTS—DISTINCTION OF ATOM, MOLECULE, AND EQUIVALENT BY LAURENT—NEW CHARACTERISTICS OF POLYBASIC ACIDS—MOLECULES OF THE ELEMENTS.

THE battle was over, and the victory won. It had been shown that, starting from the decompositions which substances undergo under the influence of the galvanic current, we are not in a position to explain the manifold reactions of organic chemistry, and in particular, the phenomena of substitution. The foundations had been shaken by the fact that positive hydrogen was replaceable by negative chlorine, and the whole edifice—the electro-chemical theory—collapsed. Organic chemistry had shown that laws which had been advanced without reference to the facts that it presented, did not harmonise with the teachings of these facts. It was now a question, however, as to whether organic chemistry could also render any positive service—whether it would be possible, starting from the facts which it had already furnished, or which it would furnish in the future, to establish new principles that might serve as the basis of a chemical system.

The way of looking at substances from the electro-chemical point of view, and dualism also, were maintained in the case of inorganic compounds. In order to do this, a sharp distinction between the latter and organic compounds became necessary, so that it might be possible to apply a doctrine to inorganic compounds which had proved inapplicable to organic compounds. If this doctrine was to be completely supplanted, however, and if organic chemistry was to enjoy the fruits of its victory, it was necessary that this younger branch of the science should offer to the opposing party definite principles upon which it might be reconstructed. It was not in a position to do this at first, since, up to this time, more attention had been paid to overthrowing the old system than to building up a new one. It is true that endeavours were made on various sides to embrace all organic compounds in one uniform conception. The radical theory, the nucleus theory, and the theory of types had arisen, and each had its supporters ; but the very fact of their being so many views, proved the insufficiency of any of them. We find, then, a great deal of confusion ; the adherents of the different systems were in continual strife, and a becoming demeanour was not always maintained.

Consequently, it is difficult to say which were the prevailing ideas at the beginning of the fifth decade of the nineteenth century. Even the views as to the principles of each mode of regarding constitution were widely at variance from one another. The school of Gmelin had greatly augmented its adherents, and to the latter the atomic theory appeared too hypothetical. We cannot be surprised to find that chemists now begin to lean more and more in this direction, since even the expression "atomic weight" is gradually supplanted by the "equivalent," and the latter is employed, as it had been by Wollaston, in the sense of combining weight.[1] Upon the overthrow of the system of Berzelius (that is to say, of the only system which, in any uniform sense, embraced the whole science), and with the origination of the most various hypotheses and theories, which were not capable of any general application and did not seem to have any promise of a long existence, there arose in the minds of many a certain aversion to all speculation, which was looked upon as premature and hurtful to the science. Nothing was in keeping with the times except the temperate consideration of observations, and Gmelin was the right man to represent a tendency of this kind. He united boundless industry with wide knowledge, and he understood how to turn both of these qualities to account in his

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[1] Compare Liebig, Annalen. 31, 36.

Hand-book. In adducing facts completeness and conscientiousness were his watchwords, and these were adhered to.

Since formulæ, for Gmelin's school, merely represented the composition of substances by means of a contracted style of writing them, these chemists were at liberty to choose their "equivalents" or "combining weights" at will from the possible multiples. The guiding principle appeared to them to be simplicity in symbolising, and therefore their numbers possess little real significance as regards development. I shall merely remark that they adopted the formulæ of Berzelius for most compounds, and, in doing so, they regarded the double atom as an equivalent. They arrived at this by halving the atomic weights of oxygen, sulphur, carbon, selenium, etc., with reference to hydrogen, chlorine, bromine, iodine, nitrogen, phosphorus, and the metals.[2]

It must not be supposed, however, that, at the beginning of the forties, the atomic weights of Berzelius were no longer used. On the contrary, they were still employed by Liebig and his numerous and important followers,[3] and it was only towards the end of the decade (after the appearance of Gerhardt's paper) that the latter also made use of Gmelin's equivalents. I have already indicated in a previous lecture what the reasons were that brought about this revolt from the atomic theory.[4] Although I said there that none of the physical rules which expressed relations between the atomic weight and certain properties of matter, appeared capable of general application, on the other hand, the law which had enabled Dalton to advance the atomic theory, that is, the law of multiple proportions, was still unattacked. The examination of numerous organic compounds whose investigation was already completed, had only tended to confirm it. No doubt, it had become necessary to admit that a much larger number of atoms can unite with one another than either Dalton or Berzelius had considered possible, and the law had, on this account, obviously to some extent lost its definite character. Even at that time the question might have been asked, whether the statement could be called a law, since chemists were not in a position to determine anything as to the limits of the power of combination of atoms; and also whether every compound could ultimately be referred to unvarying weights of the constituents, if any large multiple might be chosen at will. Ideas of this kind do not appear, however, to have arisen at that period,[5] and so there always remained this one generalisation for those who tried to retain the atomic theory and to advance speculations as to the constitution of compounds. Amongst these, Dumas had in the recent years played the most important part, by founding his theory of types. In this theory, which was no doubt, partly borrowed from Laurent, there was much that was eminently suited for a classification of organic compounds; but still the use of it was only recognised more generally after its fusion with the radical theory, that is, after radicals had been introduced into the types. This could only take place after the conception of the radical had been completely transformed, and it is now my business to show how and by whom this development was brought about.

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[2] Compare Gmelin, Handbuch. First Edition, 34. At this time Gmelin also halves the atomic weight of phosphorus, and so writes phosphoric acid P_2O_5, as Berzelius did. [3] The sign for the double atom is not employed in Liebig's Annalen., and H_2O is therefore printed instead of $\text{Ħ}O$, as Liebig observes from want of the necessary types. [4] Compare p. 106.

On studying the writings of the founders of the radical theory, one might be tempted to assert that it was they who not only established the conception of the radical in its first signification, but that, at the same time, they had also done the most important service in respect of the subsequent acceptation of the word. Thus, the following passage from Berzelius is noteworthy:—[6]

"We shall assume that, by means of any circumstance whatsoever, we could clearly see the relative position of the simple atoms in the compound atom of the salt [sulphate of copper]. It is clear that, whatever this may be, we should then find in it neither oxide of copper nor sulphuric acid, for the whole is now a single coherent substance. We can picture to ourselves . . . the elements in the atom of the salt as coupled together in various ways; for example, as one atom of sulphide of copper combined with four atoms of oxygen, that is to say, as the oxide of a compound radical; as one atom of binoxide of copper and one atom of sulphurous acid; as one atom of copper and one atom of a salt-former, SO_4; and, finally, as one atom of oxide of copper and one atom of sulphuric acid. So long as the simple atoms remain together, one of these notions is as good as another. If it is a question, however, of the behaviour when the compound atom is decomposed by electricity, or by the action of other substances (in the wet way for instance), then the relation is quite different. The compound atom in that case never undergoes decomposition in accordance with the first two views, but it does according to the two latter. The copper can be exchanged for other metals according to the view $Cu + SO_4$; but if the copper is taken away without being replaced, as is the case by the action of electricity, then that part of the atom of the salt which remains over, breaks up into oxygen and sulphuric acid. If, on the contrary, the salt of copper is decomposed either by a very feeble electrical force or by means of other oxides, into oxide of copper and sulphuric acid, both of these remain afterwards, and from them the salt can be compounded again. There must obviously be a reason for these circumstances, and the reason can scarcely be other than this, that when sulphuric acid and oxide of copper unite to form a compound atom of the salt, the relative positions of the atoms in the united binary substances do not materially change, and the latter can thus be combined or separated as often as is desired. . . . From this, however, it easily follows that in decomposing to form other binary compounds of the elements, the atoms must undergo a transposition of their relative situations, so that their capacity for combining anew is either diminished, or, as is usual, ceases entirely. Nitrate of ammonia, which is decomposed into nitric acid, ammonia, and water, and is recompounded from these, can be decomposed by heat into nitrous oxide and water, without our afterwards being able to recompound it from these substances. The reason for this fact must be that, in the latter mode of decomposition, the atoms of the elements are transposed into other relative situations which are obstructive to their reuniting."

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[5] Compare, however, Berzelius in Liebig's Annalen. 31, 17; also Dumas, ibid. 44, 66.

[6] Jahresbericht 1835, 348.

These ideas are as clear, as impartial, and as unprejudiced as could possibly be desired. The same holds also for the following statements of Liebig :[7]

"A theory is the explanation of positive facts, which does not permit us, from the behaviour of a substance in various modes of decomposition, to make deductions backwards as to its constitution, with conclusive certainty, simply because the products vary with the conditions of the decomposition.

"Each view as to the constitution of a substance, is true for certain cases, but unsatisfactory and insufficient for others."

Even if I also admit that the principles of the newer radical theory are expressed in these statements of the two great teachers,[8] still it would appear to me presumptuous that any one should declare the latter, on this account, to be the authors of the views which are now to be discussed. By their activity in other directions in the domain of theoretical chemistry, they have shown that, with them, the radical is a definite, unchanging group, and that they only considered a single view as to the constitution of compounds to be admissible. I would recall the numerous discussions regarding the conceptions of alcohol and its derivatives. Would these have been possible if opinions such as those quoted above had been guiding and predominant ideas with Berzelius, Liebig, and Dumas? Prior to the discovery of the phenomena of substitution, this certainly was not the case. In treating of Berzelius and of Dumas, we have already discussed the influence which these facts exerted upon the conception of the radicals. We have still got to consider

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[7] Annalen. **26**, 176-177.

[8] Thus Gerhardt, for example, begins the exposition of his theoretical views by directing attention to the various formulæ that are possible for sulphate of baryta; that is to say, he adduces considerations quite similar to those quoted above as advanced by Berzelius. See Gerhardt, Traité de Chimie. 4, 561.

Liebig's relations to them. His opinion concerning Laurent's nucleus theory must not guide us here. The discovery of trichloracetic acid had not been without effect upon him also, and he not only admits the replaceability of hydrogen by negative elements, but he also agrees with Dumas in his views respecting these facts. This is seen from the following :[9]

"The remarkable observation has been made in inorganic chemistry, that the manganese in permanganic acid may be replaced by chlorine without altering the form of the compounds which permanganic acid can produce with the bases. There can scarcely be a greater dissimilarity in chemical properties than that between manganese and chlorine. . . . Chlorine and manganese can replace each other in certain compounds without alteration in the nature of the compounds. I do not see why a similar behaviour should be impossible with other substances—with chlorine and hydrogen, for example, and this very view of these phenomena, in the form in which it has been advanced by Dumas, appears to me to furnish the key to most of the phenomena of organic chemistry."

Dumas, it is true, goes too far for him. Liebig will not admit, for example, the replaceability of carbon, and he prints in his journal the well-known letter of S. C. H. Windler[10] which makes sport of Dumas in a somewhat harsh manner. However this may be, it might appear from these statements that Liebig had materially contributed by his views to the further development of the radical theory. This is not my belief, and I find support for my view in a paper on the theory of ether, which he published in the year 1839.[11] Liebig here endeavours to solve the difficulties of the question as to the constitution of ether, by the assumption of the radical acetyl ; and, in doing so, he proves to us that radicals, with him, still retain their old signification. The whole plan of his Handbook also shows the same thing.[12]

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[9] Annalen. 31, 119, Note. [10] Ibid. 33, 308. [11] Ibid. 30, 129; compare p. 137. [12] See Liebig's Handbuch der Chemie, Heidelberg (1843), especially 2, 1, etc.

In my opinion, the labours of Laurent and of Gerhardt chiefly contributed to make the radical what it still is. Laurent, by advancing the nucleus theory, emphasised the variability of the radicals, a matter that was afterwards brought forward by Dumas also.[13] But it was Gerhardt who first indicated the possibility of the assumption of two radicals in one compound, and thereby destroyed all idea of the actual existence of separated groups. It is with the history of this part of the development of organic chemistry that we are now concerned.

The influences of his gifted teacher, Liebig, can scarcely fail to be observed in Gerhardt's earliest publications. We are aware that Liebig disputes the presence of water in the acids. By a very happy extension of the idea, Gerhardt negatives the pre-existence of water in the majority of organic compounds. Its presence in alcohol, especially, appears to him just as unlikely as that of ammonia in the substances containing nitrogen from which ammonia is evolved by means of potash. He knows that there is a class of substances of simple composition and of extraordinary stability, such as water, carbonic acid, hydrochloric acid, and ammonia, some of which are produced in almost every organic decomposition, without, however, our being able to recompound, from these substances, the substances originally decomposed.[14]

The formation of one substance out of another was not, with Gerhardt, any ground for the assumption that the first was present in the second, ready formed : substances do not require to contain any water in order that water may be separated from them in certain reactions. The reason for the frequent formation of water and similar substances is to be found in their stability, and in the great affinity which their constituents possess for one another. Now this view was of essential significance, and it led Gerhardt, in 1839, to the theory of residues and of coupled compounds.[15] He says[16] that when two substances react upon each other, an element

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[13] Compare pp. 146 and 167. [14] J. pr. Chem. **15**, 37. [15] Ann. *Chim. [2]* **72**, 184. [16] Comptes Rendus. **20**, 1031.

(hydrogen) separates out from the one, and unites with an element (oxygen) from the other to produce a stable compound (water), whilst the residues join together. Mitscherlich's nitro-benzene[17] is to be regarded, according to Gerhardt, as produced in this way out of a residue of benzene and a residue of nitric acid. The hydrocarbon gives up hydrogen, and the nitric acid gives up oxygen. Sulphobenzide[18] is also regarded in the same way; it contains the residues $C_{24}H_{10}$ from the benzene, and SO_2 from the sulphuric acid.[19] The SO_2 in this case is not identical with sulphurous acid, as the latter occurs, for instance, in sulphite of lead, but it is contained in the compound in quite a special form, namely as a substituted group.

Although this latter view is a very peculiar one, still it was eminently suited to supplant the belief in the pre-existence of radicals. The residues were imaginary substances, which were all the more completely deprived of any reality by the fact that they were assumed to be different from the similarly composed atomic groups which occurred in the free state.

About two years later (in 1841) Mitscherlich[20] propounds similar ideas, which, however, he extends to a much larger class of substances. According to him, also, compounds do not contain any ready-formed radicals which play the part of elements in decompositions; in the appearance of water, he sees the reason for the observed direction taken by decompositions; and therefore he does not seek for this reason in the constitution of the substances employed. The products which are obtained by the action of acids upon bases or alcohols (salts and esters), are likewise considered from this point of view, and it is shown that they decompose again into their constituents by taking up water.

The idea of the residues was well adapted to explain the phenomena of substitution; the latter, according to Gerhardt, obeyed the following rule.[21] The element eliminated is replaced either by an equivalent of another element, or by the residue of the reacting substance. The application of this rule was limited, however, for Gerhardt, besides substitutions, is also acquainted with additions, and these of two kinds. Firstly there are those in which the saturating capacity is altered, and the formation of salts is reckoned amongst these ; and then there are additions in which this is not the case. Gerhardt directs his attention chiefly to the products of the latter kind of addition, and calls them coupled compounds (*corps copulés*). To this class there belong, in particular, the substances produced by the action of sulphuric acid upon organic compounds, such, for example, as benzoyl sulphuric acid and its salts, discovered by Mitscherlich.[22] The acid is produced by the action of sulphuric acid upon sulphobenzide. According to Gerhardt, the two substances become coupled, whereby the saturating capacity of sulphuric acid, which was still regarded at that time as monobasic, remains unchanged. Thus :—

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[17] Pogg. Ann. 31, 625. [18] Compare Mitscherlich, Pogg. Ann. 31, 628. [19] Dumas' atomic weights: C=6, O=16, S=32 etc. [20] Pogg. Ann. 53, 95. [21] Ann. Chim. [2] 72, 196.

$$\underset{\text{Sulphobenzide.}}{C_{24}H_{10}(SO_2)} + \underset{\text{Sulphuric acid.}}{SO_3H_2O} = \underset{\text{Hyposulphobenzidic acid.}}{C_{24}H_{10}(SO_2)\ .\ SO_3\ .\ H_2O.}$$

Sulphovinic acid (ethyl sulphuric acid) is regarded as a coupled compound of sulphate of ethyl and sulphuric acid, and is written $C_8H_{10}(SO_2)O_2.\ SO_3H_2O$; whereas sulphobenzoic acid, the basicity of which is supposed to be equal to the sum of the basicities of its constituents, and in the formation of which the saturating capacity has remained unchanged, is reckoned amongst the conjugated acids, a class of substances which were first distinguished by Dumas.[23] It may, however, also be regarded as produced by the coupling of a substituted benzoic acid, $C_{28}H_{10}(SO_2)O_4$, with sulphuric acid.

The view announced above with respect to coupled substances, is very soon abandoned by Gerhardt. He retains the name, but gives it a different signification. But I have intentionally stated the older notion, because the word was also employed by Berzelius and by Kolbe, who again bestowed a special signification upon it. It appeared to me of interest to follow the historical course of an expression which has been employed in senses so numerous and so varied.

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[22] Pogg. Ann. 31, 283 and 634.

[23] Dumas and Piria, Annalen. 44, 66 ; Ann. Chim. [3] 5, 353.

Gerhardt, in 1843, regards all compounds as coupled which are prepared by the action of acids upon alcohols, hydrocarbons, etc., and in whose formation the substances unite with the elimination of water.[24] Coupled compounds were, accordingly, no longer addition products, obtained by the union of two compounds, but they were formed by the joining together of two residues. They were, therefore, substitution products—a view which Gerhardt, however, does not adopt. With him, they still constituted a special class and were not compared with the original substances, principally, no doubt, because they possessed a different saturating capacity. With respect to the latter also, Gerhardt has now become of a different opinion, and states that the basicity of the coupled compound is equal to the sum of the basicities of the substances coupled, less one. From this statement, which is advanced as an axiom, the dibasic character of sulphuric acid follows. Coupled with neutral substances, such as alcohols, or hydrocarbons, sulphuric acid gives rise to monobasic acids, whereas acetic acid, nitric acid, hydrochloric acid, etc., do not possess this property, and are hence regarded by Gerhardt as also monobasic.

In 1845, Gerhardt endeavours to show the general applicability of the law of basicity mentioned above.[25] He now designates as coupled, all compounds which are formed by the union of two substances with the elimination of water and decompose into their constituents again by taking up water; and, therefore, he reckons in this class, the neutral ethers, the acid ethers, etc., and formulates the law

$$B = (b + b') - 1,$$

where B represents the basicity of the coupled compound, and b and b' the basicities of the substances which take part in its formation. Gerhardt expressly remarks here that this equation holds only for the coupling of a single equivalent,[26] and that the equation must be applied twice in order to ascertain the correct basicity of the product obtained by the coupling of two equivalents of one substance with one of another. Thus sulphuric acid, for example, which Gerhardt now regards as dibasic, can form with neutral substances both acids and neutral products. The ether of sulphuric acid belongs to the latter class of substances; it is produced from two equivalents of alcohol and one equivalent of acid. Its basicity, B, is obtained from the following equations, in which B_1 represents the basicity of ethyl sulphuric acid :—

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[24] Comptes Rendus. 17, 312.

[25] Comptes rendus des travaux chimiques par Laurent et Gerhardt, 1845, 161.

$$B_1 = (2 + 0) - 1 = 1$$
$$B = (1 + 0) - 1 = 0.$$

Strecker, in 1848, thought he had brought the rules into a more general form when he made a statement to the following effect :—[27] The basicity of the coupled compound is equal to the sum of the basicities of the compounds, less one-half of the number of hydrogen equivalents removed,[28] or the basicity is diminished by one unit for each pair of hydrogen atoms removed. But in this way of stating the matter, the same result as was required by Gerhardt's rule was, necessarily, always obtained. It can only be regarded as a simplification (not as a wider generalisation) in which a single application was sufficient in all cases.

Although it was afterwards shown that even this form of the law of basicity does not always lead to accurate conclusions,[29] and although the exceptional position which was given to certain classes of substances in consequence of the idea of coupled compounds, was more recently recognised as incorrect,[30] still, it cannot be denied that the assumption of the copula played a definite part in the historical development of chemistry. In particular, these views led to new characteristics for the recognition of polybasic acids, and this was of great importance at that time, when so few of these acids were known.

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[26] Gerhardt at that time employed the word equivalent in Gmelin's sense, so that for us it often means atom and often molecule. [27] Annalen. **68**, 51. [28] Strecker assumes the equivalent of water = 9, compared with that of hydrogen chosen = 1. [29] Compare Becketoff, Bulletin phys.-math. de l'Académie de St Petersbourg, **12** (1854), 369. [30] Compare Kekulé, Annalen, **104**, 130.

The underlying idea with respect to coupled substances, that the majority of compounds could be regarded as made up of the residues of other substances, was of very great value for the progress of the science, simply because it was opposed to the rigidity and immutability of the radicals. How fertile these ideas were is shown, for example, by the discovery of the anilides and the anilid-acids.

According to Gerhardt the amides are to be looked upon as compounds of the residues of ammonia and of acids; thus he supposes oxamide to be formed according to the equation:[31]

$$C_2H_2O_4 + 2NH_3 = C_2H_2O_2 \cdot (NH)_2 + 2H_2O \; [C = 12, O = 16],$$

that is to say, by the replacement of two oxygen atoms by twice the imid- residue NH. Regarding a similar replacement as also possible by means of the residue of aniline, the nature of which had been settled by Hofmann's comprehensive and interesting researches,[32] and then trying to show this replacement by direct experiment, he succeeds in preparing oxanilide, the formation of which is represented by the following equation:

$$C_2H_2O_4 + 2C_6H_7N = C_2H_2O_2 \cdot (C_6H_5N)_2 + 2H_2O.$$

He carries the analogy between ammonia and aniline still further by the discovery of the anilid-acids, which he regards as analogous to the amid-acids.[33] Thus he writes the formula of sulphanilic acid, which he obtains by the action of sulphuric acid upon oxanilide, $SH_2O_3 . C_6H_5N$, and, in its existence, finds a new proof of the dibasic character of sulphuric acid.

It may perhaps seem strange that Gerhardt introduces the residues NH and C_6H_5N into these compounds, instead of NH_2 and C_6H_6N. In this he may have been influenced by Laurent, who had already tried, a few years previously, to replace the amid- by the imid- group.[34] Gerhardt was able to associate himself with this conception without involving himself in any further consequences, since his formulæ did not attempt to express the arrangement of the atoms but were only contracted equations. They were not intended to represent what the compounds are, but merely what their nature is and what becomes of them:[35] they were meant to indicate the modes of formation and of decomposition of substances. Gerhardt was the first to advance the view that we should not conclude from the decomposition products as to the arrangement of the atoms, because the latter are set in motion by the reaction.[36] According to him, several formulæ were therefore possible for the same substance, and different residues (radicals) might be assumed in it according to the decompositions which it was desired to emphasise. In this way the point of the controversy, which had been carried on so fiercely and so long, as to the nature of the radicals, was demolished. Afterwards, Gerhardt comes to employ empirical formulæ, which had been recommended by Liebig on account of the constantly growing divergences of opinion as to rational constitution.[37] Conjointly with Chancel, he introduces, in 1851, the synoptic formulæ,[38] which never met with any general acceptance because they were inconvenient and not easily understood. If the form was new, still the idea was simply the old one. This mode of writing formulæ was likewise intended only to represent the formation and decomposition of substances, and it too consisted of contracted equations. The great advantage of this way of regarding the matter lay in the possibility of advancing several rational formulæ for one substance, whereby new analogies and differences made their appearance and gave rise to a large number of investigations.[39]

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[31] Comptes Rendus. **20**, 1032. [32] Annalen. **45**, 250; **47**, 37. [33] Journ. de Pharm. [3] **9**, 405; **10**, 5; compare Annalen. **69**, 308.

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[34] Comptes Rendus. **1**, 39. [35] Gerhardt, Introduction à l'étude de la Chimie, 1848. [36] Compare Baudrimont, Comptes Rendus. 1845. [37] Annalen. **31**, 36. [38] J. pr. Chem. **53**, 257. [39] It may be remarked here, in passing, that Gerhardt, a few years later, again replaces imid, NH, by amid, NH_2, after Laurent (J. pr. Chem. **36**, 13), in 1844, had adopted and sought to establish Hofmann's conception of aniline as phenamid.

Gerhardt's activity was perhaps of still greater importance in connection with another question; that is, with the fixing of the atomic and molecular weights. Although the movement for the revision of these most important numbers originated with him alone, still he was influenced in the further elaboration of the work by Laurent, with whom he was at that time in very intimate communication. Indeed, I might almost say that it was Laurent who first clearly stated[40] what Gerhardt wished to advance. It is, however, extremely difficult to separate from one another the services of the two chemists, because they published a great deal conjointly, and probably discussed everything together. I would ask, therefore, that my statements with respect to this matter may not be taken too literally.

Gerhardt's first paper on the subject in question dates from the year 1842.[41] In this paper he frequently employs the word equivalent in a sense in which it was introduced into chemistry by Wollaston and Gmelin, although this sense is one of which we cannot any longer approve. With Gerhardt the word is one whose signification he does not seek for in its origin, otherwise he could not call H_2SO_4 and HCl one equivalent each; for he himself wishes to prove that sulphuric acid is dibasic, in which case it is not equivalent to hydrochloric acid. What Gerhardt wishes to determine are atomic and molecular weights, which, however, he does not yet understand how to distinguish from each other, and for which he uses the word "equivalent," at the same time designating as "atomic weights" the numbers which he is attacking.

Gerhardt's equivalents, so-called, are not really equivalent, but merely comparable quantities; and in determining them, the most various points of view which can be of consequence in estimations of atomic and molecular weights and of equivalents, are taken into consideration.

It must appear striking and peculiar to any unprejudiced person, that the numbers which Gerhardt proposes as the

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[40] Ann. Chim. [3] **18**, 266.

[41] J. pr. Chem. **27**, 439; also Ann. Chim. [3] **7**, 129; **8**, 238.

"equivalents" of the elementary substances (with the exception of the numbers for the metals), agree almost completely with the atomic weights of Berzelius, of the year 1826. It is also noteworthy that Gerhardt does not mention Berzelius, and is obviously quite unaware that he, to a large extent, adopts his numbers. On the other hand, the Swedish chemist does not appear to have noticed this agreement, since he violently attacks Gerhardt's paper.[42] What I consider as most remarkable, however, is the fact that, at the time when Gerhardt makes his proposal, very eminent chemists (I only mention Liebig and his pupils[43]) are actually employing atomic weights for the most important elements, such as carbon, oxygen, hydrogen, chlorine, etc., with the ratios which Gerhardt recommends as new; but that, a few years afterwards, the equivalents of Gmelin, against which Gerhardt's paper was directed, are almost universally adopted.

The valuable part of Gerhardt's paper consisted, however, much less in the suggestion which he makes as to the "equivalents" of the elements, than in his views respecting the equivalents of compounds. In following up, by means of equations, the decompositions of organic substances, he arrives at the general proposition that the quantities of carbonic acid, water, and ammonia produced in these decompositions are expressible as multiples, by whole numbers, of C_2O_4, H_2O_2, and NH_3.[44] Hence, according to him, these quantities must represent an equal number of equivalents, whereas it was at that time assumed that the equivalents of carbonic acid and of water were only half as great as these formulæ would indicate.

Guided by quite similar considerations, he fixes the equivalents of carbonic oxide and of sulphurous acid as C_2O_2 and S_2O_4, and, in doing so, adds, as an important support of his assumptions, that these quantities occupy exactly the same space in the gaseous state. He is thus able to assert that the equivalents of carbon, oxygen, and sulphur are not 6, 8, and 16, as Gmelin's school assumed, but twice these numbers, that is, 12, 16, and 32; and he proves, by many examples, that there do not exist any equivalent formulæ, constructed on the principles advanced by himself, which contain less of the respective elements than these latter quantities. He also proves that an even number of atoms of carbon, of oxygen, and of sulphur always occurs in compounds containing these elements, if they are represented by means of Gmelin's equivalents.

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[42] Berzelius, Jahresbericht 1844, 319. [43] Liebig (Annalen. 31, 36) points out that it will probably never be possible to ascertain the true atomic weights, and that it is therefore better to employ the equivalents.

[44] $C=6$, $O=8$, $N=14$, $H=1$.

Consequently Gerhardt doubles the equivalents of carbon, of oxygen, of sulphur, etc., with reference to those of hydrogen, of chlorine, of nitrogen, etc., whereby he obtains Berzelius' numbers. He differs very materially from the followers of Berzelius in the formulæ which he proposes for organic compounds. According to him, these had been doubled, as compared with many inorganic substances, consequently he halves them; they were, as he expresses it, referred to $H = 2$, or to $O = 200$, whilst, for the majority of inorganic compounds, the number chosen for comparison was $H = 1$ or $O = 100$. Hence substances were divided into those like water, carbonic oxide, carbonic acid, etc., which occupy two volumes ($H = 1 = 1$ vol.), and those like alcohol, ethylene, chloride of ethyl, etc. (that is, all the substances which were then called organic, and of which the vapour densities were by no means always known), which correspond to double this volume.

I may be permitted to leave off the consideration of Gerhardt's views here, in order to glance backwards and seek for the reasons which had caused chemists to write "four-volume" formulæ for organic substances. This way of writing them must appear all the more remarkable since both Berzelius and Dumas, at first, at least, believed that they must choose the atomic weights of compounds so that they should represent equal volumes in the state of vapour.

Relatively few vapour densities were known at that time, and hence the rule was broken in many cases without the fact being known. Another very important reason lay in the widely spread assumption that the acid was the substance united to the base in a salt, or, as it can also be expressed, that the usually hypothetical anhydrides (instead of the hydrates) were regarded as acids. Thus, on the basis of the atomic weights of Berzelius, the analysis of acetate of potash led to the formula $K.C_4H_6O_4$, and from this, after deduction of the potash, KO, the atom of acetic acid remained as $C_4H_6O_3$, which did not permit of any further division. Those who regarded atom and equivalent as identical had to find confirmation of the accuracy of this formula in the fact that this quantity of acetic acid is neutralised by one equivalent of potash, KO ; and so the formulæ of all monobasic acids were necessarily doubled. The establishment of the theory of polybasic acids caused Liebig to double the formulæ of several dibasic acids, as for example, that of tartaric acid (see p. 159). This, in turn, affected the atomic magnitudes of neutral substances, such as alcohol, compound ethers, etc. To the first of these the formula C_2H_6O, corresponding to two volumes, had at first been assigned, and, in order to arrive at this formula, Berzelius assumed a radical in alcohol different from that in ether.[45] But Liebig, with whom alcohol was the hydrate of ether, adopted the group ethyl, C_4H_{10}, as the basis of both,[46] and the close relations between alcohol and acetic acid then became prominent for the first time. Ethylene was now written C_4H_8, and chloride of ethyl $C_4H_{10}Cl_2$; that is to say, all the compounds of the ethyl series contained four atoms of carbon. Quite similar reasons caused the doubling of the other formulæ.

Gerhardt wishes, as we have stated, to halve these, and he is moved to do so from other points of view besides that of the volume relations. According to him, the salt-forming metallic oxides do not consist, as Berzelius assumes, of one atom of metal and one of oxygen, but they are comparable with water (which he now writes H_2O) and contain two atoms of metal ;[47] whereas in the hydroxides one atom of metal and one of hydrogen are united with one atom of oxygen.[48] He is therefore obliged to halve the atomic weights of the metals, and to assume K = 39, Na = 23, Ca = 20, etc. He calls that quantity of a monobasic acid an equivalent which yields a neutral salt by the replacement of one part of hydrogen by 39 parts of potassium, whilst he assumes the equivalents of the dibasic acids to be twice that quantity.[49] The formula of acetic acid therefore becomes $C_2H_4O_2$ while that of oxalic acid, $C_2H_2O_4$, remains unchanged.

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[45] Compare p. 132. [46] Compare p. 133. [47] Compare also Griffin, Chemical Recreations, Seventh Edition (1834), 92-93 and 228-229. [48] Ann. Chim. [3] 18, 266.

That Gerhardt, in spite of these well-considered and excellent observations, which are now for the most part adopted, had not reached the point of view which we take up, is shown by a part of his paper[50] where he thinks he should point out that, as a consequence of his proposals, the atomic theory, the theory of volumes, and the equivalent theory all coincide. According to our present views this is not attainable. The various conceptions were first separated from one another in 1846, by Laurent,[51] who thereby rendered Gerhardt's numbers admissible. He showed that these values were not by any means equivalent, and consequently did not deserve the name. They express, as he points out, those quantities which enter into reaction, and accordingly represent molecular weights.

Although Gerhardt's endeavours in the determination of equivalents tended in the direction of employing comparable quantities only, this was first stated and elevated to a principle by Laurent. According to the latter, it is necessary to start from a "*terme de comparaison*" and to refer the formulæ of all compounds to it. Since he is quite clear as to the fact that the quantities contained in equal volumes do not always produce the same chemical effect, he considers the question whether he will compare substances in the gaseous state according to the space which they occupy, or whether he will compare their equivalents. He rejects the latter comparison, on account of the difficulty associated with the determination of equivalents of substances which are not analogous, and decides in favour of the first comparison; that is to say, he chooses the formulæ (and therefore the molecules) of substances so that they represent two volumes ($H = 1 = 1$ vol.) in the state of vapour. In doing so he is obliged, however, to admit certain exceptions to which he draws attention. Thus it was known from Bineau's investigations[52] that the formulæ NH_4Cl, for sal ammoniac, and SO_4H_2, for sulphuric acid,[53] correspond to four volumes, but, in spite of this, these quantities are regarded by Laurent as representing their molecular weights. There were definite grounds, in these instances, which appeared to make this assumption necessary. The isomorphism of sal ammoniac with potassium chloride excluded the formula $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$; the dibasic character of sulphuric acid, which Laurent looked upon as proved, demanded a molecular weight at variance with Avogadro's hypothesis. Even if this hypothesis, therefore, was regarded as the chief standard in the fixing of formulæ, still the results obtained were subject to modification by chemical reactions, and by physical properties such as specific heat, specific volume, crystalline form, etc. Further, the law of the even number of atoms, which had been outlined for special cases by Gerhardt[54] in 1843, played an important part in these determinations. Laurent now states this law, to the effect that in all compounds the sum of the atoms of hydrogen, chlorine, bromine, nitrogen, etc., must always be an even number. The law becomes of increased significance from the fact that Laurent applies it in order to prove that the molecules of these elements, which he calls dyads, consist of two atoms.[55]

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[49] Ann. Chim. [3] 7, 129. [50] Ibid. [3] 7, 140. [51] Ibid. [3] 18, 266.

Gerhardt's ideas were greatly elucidated by Laurent, who made them more generally accessible and comprehensible by laying greater weight upon the terms he employed, and by defining these terms precisely. As a result of this, an important advance was effected, because the separation of atom, molecule, and equivalent was now really accomplished; and hence it again became possible to employ Avogadro's hypothesis (thirty-five years after its promulgation) as the basis of a system. With Laurent, the molecule is the smallest quantity of a substance which is required in order to give rise to a compound, and which, in the form of vapour, always (or at least with few exceptions) occupies double the volume of an atom of hydrogen. The atom is the smallest quantity of an element which occurs in compounds, whilst the equivalents represent quantities of analogous substances which have the same value in reactions.[56]

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[52] Ann. Chim. [2] **68**, 416. [53] Compare ibid. [3] **18**, 289. [54] Ibid. [3] **7**, 129. [55] Ibid. [3] **18**, 266; compare also Laurent, Méthode de Chimie. 77; **E.** 62.

I shall try to give an idea of the importance to chemistry of these definitions, by stating some of the conclusions that were drawn from them in view of the experimental work of the period.

The consistent application of the idea of equivalents necessitated the assumption by Laurent and Gerhardt of several equivalents for many of the metals.[57] "The idea of the equivalent includes the notion of an identity of function; we are aware that one and the same element can play the part of two or of several others, whence it must occur that different weights also correspond to these different functions. On the other hand we find different weights of the same metal, such as iron, copper, mercury, etc., replacing the hydrogen of acids, and, in doing so, forming salts which contain the same metal but possess different properties. These metals have, consequently different equivalents."

This idea was not new,[58] but as really equivalent formulæ had never been employed, it had not up to this time had any further consequences. Now, when Laurent and Gerhardt introduce this mode of writing formulæ, it acquires a certain value. Thus, for example, these reformers of chemistry seek to find analogies where they had hitherto remained concealed; the formulæ of the sesquioxides can be assumed to be similar to those of the normal bases, and a uniformity can thus be introduced into the way of regarding salts which has not been possible hitherto. It is known that the neutral sulphate of the protoxide of iron (ferrous sulphate) contains, for the same quantity of sulphur, one and a half times as much iron as the neutral sulphate of the peroxide of iron (ferric sulphate). Thus we may express it that 28 parts of iron in the ferrous salt can take the place of one part of hydrogen, while the latter can also have its place taken by $18\frac{2}{3}$ parts of iron, in the ferric salt; both quantities are, therefore, equivalent to one part of hydrogen. If we distinguish, as Laurent and Gerhardt did, by the terms *ferrosum* ($Fe = 28$) and *ferricum* ($fe = \frac{2}{3}.28$) the equivalents of iron in the ferrous and in the ferric salts respectively, then the formulæ of ferrous sulphate $(Fe_2)\,SO_4$ and of ferric sulphate $(fe_2)\,SO_4$ become comparable with each other. A similar thing holds for other metals such as copper, mercury, tin, etc.; in the salts corresponding to the lower and to the higher oxides of these metals, different equivalents, of which the one is double the other,[59] must be assumed in each case.

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[56] Ann. Chim. [3] 18, 296; also Comptes rendus des travaux chimiques par Laurent et Gerhardt, 1849, 257. [57] Ibid. 1849, 1, etc. [58] Compare p. 103.

Complete analogy is attained in the mode of writing salts when equivalent formulæ are employed for acids also. We then have :—

Ferrous sulphate	Cupric chloride	Mercurous chloride
$SO_4\,(Fe_2)$	$Cl_2\,(Cu_2)$	$Cl_2\,(hg_2)$

In this mode of writing formulæ, the differences between monobasic and polybasic acids disappear; and it certainly is an advantage of the molecular formulæ that they permit these highly important peculiarities to become prominent. Laurent and Gerhardt recognised this very fully, and it was the latter, especially, who endeavoured, and with much success, to bring about the separation of these classes of substances by more definitely advancing new characteristics.[60]

The formation of double salts with non-isomorphous bases did not appear to Gerhardt sufficient for fixing the basicity of an acid; he points out that dibasic (and polybasic) acids can form two (and more) ethers, of which one (or more) is acid, and one is neutral. The molecule of the latter, if it is assumed to correspond to two volumes, contains one alcohol residue in the case of monobasic acids, and two (or several) such residues in the case of dibasic (or polybasic) acids. Further, the amid-compounds, and also the anilid-compounds (discovered a short time previously[61]) furnish additional evidence. Thus whilst the monobasic acids produce only one amide, one nitrile, and one anilide, the acid ammonium salts of dibasic acids, by the loss of water, give rise to the formation, besides, of an amid-acid and of an imide ; and they alone can yield anilid-acids.

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[59] Laurent's views with respect to the mode in which the existence of several equivalents for the same element may be explained are given in his Méthode de Chimie, 127; E. 103.

[60] Laurent and Gerhardt, Comptes rendus mensuels des trauvaux chimiques, 1851, 129; J. pr. Chem. 53, 460.

Laurent had already drawn attention, a few years earlier, to another difference between these substances.[62] According to him, only the formulæ of the dibasic and polybasic acids permit the assumption of their containing water, whereas in one molecule of a monobasic acid the constituents of only half a molecule of water require to be present, for which reason, the latter are not able to form anhydrides.

Thus nitric acid is :—$HNO_3 = (HO_{\frac{1}{2}}) + NO_{2\frac{1}{2}}$; while sulphuric acid is :—$H_2SO_4 = H_2O + SO_3$.

With Laurent, hypochlorous anhydride, which was already known at that time, is ClHO in which one atom of hydrogen is replaced by one atom of chlorine.[63]

Laurent's views as to the molecules of the elements were also very important. It was a consequence of Avogadro's hypothesis, with which Laurent identifies himself,[64] that the molecules of certain elementary substances should be regarded as composed of at least two atoms. Laurent tries to support this view by means of chemical reasons. According to him the so-called "dyads," such as hydrogen, chlorine, bromine, iodine, nitrogen, phosphorus, arsenic, and antimony, always occur in even numbers only; and this rule, if it is to hold for the molecules of the elements as well, renders the existence of single atoms in the free state impossible. Besides this, Laurent brings forward the well-known effects of the nascent state, and explains them by the assumption that at the moment of the separation of the elements from their compounds the single atoms are isolated, and therefore combine far more easily with others than in those cases where it is a question of molecules or of atomic groups which must first be decomposed before reaction can take place.

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[61] Compare p. 185. [62] Ann. Chim. [3] 18, 266. [63] These views were looked upon as refuted by Gerhardt's discovery of acetic anhydride etc., but strictly speaking, they were not. It was, in fact, an extension of the word anhydride to apply it to the substances discovered by Gerhardt. The relation between $C_2H_4O_2$ and $C_4H_6O_3$ on the one hand is not quite the same as that between $C_4H_6O_4$ and $C_4H_4O_3$ on the other. [64] He does not seem to be aware, however, that it was first announced by Avogadro.

Laurent and Gerhardt, with their far-reaching reforms, met with almost no immediate recognition; on the contrary, it seems as if the conception of the equivalent, in its first uncertain form, had now found more adherents than formerly, and as if Gay-Lussac's law of volumes appeared to chemists to be less adapted than ever to constitute the basis of a system. For this reason there was not, in general, the slightest tendency exhibited to assume, with Laurent, the divisibility of the molecules of the elements. It is no doubt true that urgent grounds, and especially, chemical grounds, were still wanting. It was a very happy idea that Laurent and Gerhardt had hit upon when they stated that the formulæ of substances must represent comparable quantities; but the standard was still wanting. The spaces occupied by the gases were known only in relatively few instances, and even amongst these there were some cases where the molecular weights deduced were unserviceable because they were at variance, or at least they appeared to be at variance, with the chemical properties. A series of facts which confirmed these ideas, and eventually procured for them general recognition, was still wanting. We are indebted for our knowledge of them to Williamson, who showed how to find the molecular weight by chemical methods, and thereby rendered a service to our science which cannot be too highly estimated. Even although he did not instigate the reform of chemistry, still it was his investigations which first made its accomplishment necessary and possible.

LECTURE XI.

REASONS FOR THE ASSUMPTION OF THE DIVISIBILITY OF ELEMENTARY MOLECULES—FIXING OF THE MOLECULAR WEIGHTS, BY WILLIAMSON, BY MEANS OF CHEMICAL REACTIONS — THEORY OF THE FORMATION OF ETHER—FUSION OF THE RADICAL THEORY WITH DUMAS' TYPES—SUBSTITUTED AMMONIAS—POLYATOMIC RADICALS —GERHARDT'S THEORY OF TYPES AND SYSTEM OF CLASSIFICATION.

IT has often been stated that chemistry should advance by development from within itself alone, and that the influence of the other sciences is injurious if it is exerted in any other direction than that in which chemical facts appear to lead us. I understand perfectly well that in chemistry a theory is not chosen which is in contradiction to certain facts, in order to attain a more complete agreement with physical laws, and I appreciate this from the didactic point of view in particular; but I consider it just as proper and essential in our science to modify our views so as to produce harmony with recognised natural laws, and also with theories and hypotheses, as soon as the facts permit of our doing so. It therefore appears to me appropriate, now when in our historical development we have arrived at the middle of a far-reaching reform, to advance some of the not exclusively chemical reasons which told in favour of the system of Laurent and Gerhardt. In doing this, I confine myself to facts which appear to support the divisibility of the molecules of the elements, for the special reason that this hypothesis, even after it had been repeatedly announced, still met with no approval.

Amongst the results, of extreme value in chemistry, which Favre and Silbermann announced in 1846 in their research on heats of combustion,[1] there is a very remarkable fact which deserves to be stated here. They observed that on burning carbon in oxygen, less heat is produced than when nitrous oxide is employed. They considered that this striking fact could only be explained on the hypothesis that in both cases, besides the formation of carbonic anhydride, a decomposition took place; that is to say, a change occurred involving the separation of atoms which had previously been combined. Accordingly they thought that even in the free particles of oxygen gas, several (two) atoms must be assumed, and that the quantity of heat required for their decomposition must be greater than that required for the separation of the oxygen from the nitrogen in nitrous oxide.

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[1] Comptes Rendus. **23**, 200.

By the application of a hypothesis relating to chemical combination and decomposition, Brodie[2] arrives at the divisibility of molecules of hydrogen and of oxygen. It appears to him that the contrast which was drawn, in accordance with the views prevailing at that time, between the formation of compounds and the separation of elements, has no natural foundation. In his view, every combination is merely the consequence of a decomposition, and this can only be occasioned by new combinations. He tries to prove the accuracy of this view by means of various examples, and, in doing so, introduces certain signs and expressions designed to give an idea of the contrast (more generally, of the relation) between the atoms entering into combination. According to Brodie, there exists between these a relation (polarity) of such a kind that the one is designated as positive or negative as contrasted with the other. This relation, which Brodie also calls chemical difference, depends upon the peculiarities of all those particles with which the atom is for the time being combined.

To permit of a better comprehension of this, I give here some of the examples adduced by Brodie. Silver does not unite directly with oxygen, whereas silver chloride is decomposed by boiling with potash, silver oxide being formed. According to Brodie, this is due to the fact that it is only by their combination with chlorine and potassium respectively that the silver and oxygen acquire the polarity necessary for their combination. He writes :—

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[2] Phil. Trans. 1850, 759.

$$\overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}} = \mathrm{AgO} + \mathrm{KCl}.$$[3]

According to Faraday,[4] perfectly dry calcium carbonate is not decomposed even at the highest temperatures, whereas in the presence of water the decomposition begins at once ; and similarly, according to Millon,[5] sulphuric anhydride can be distilled over carbonate of potash, the formation of a salt only taking place on the addition of water. Brodie writes :—

$$\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{SO_4}} = \mathrm{HO} + \mathrm{KSO_4}.$$

In this case, especially, it can be distinctly recognised why Brodie considers that combination is always accompanied by decomposition, whilst the first example seems to justify the converse statement. But the existence of free elementary atoms is incompatible with this, so that Brodie is at pains to show that these always appear in pairs, and then unite with one another. The most striking of the examples which he adduces is that of the evolution of hydrogen which takes place when copper hydride, discovered by Wurtz,[6] is treated with hydrochloric acid :—

$$\overset{+}{\mathrm{Cu_2}}\overset{-}{\mathrm{H}} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{Cl}} = \overset{+}{\mathrm{Cu_2}}\overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{H}}.$$

That a similar evolution is not observed on treating the metal with the acid is looked upon as owing to the fact that the same species of polarity is always associated with the hydrogen in hydrochloric acid, whilst the affinity of copper for chlorine is not sufficient to decompose hydrochloric acid.[7]

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[3] H=1, O=8, K=39, Ag=108, C=6, etc.

[4] The statement is now regarded as erroneous ; compare Gay-Lussac, Ann. Chim. [2] 63, 219.

[5] I have been unable to find this fact, quoted by Brodie, in Millon's papers.

[6] Annalen. 52, 256.

[7] Compare Wurtz, Leçons de philosophie chimique, 64.

The formation of nitrogen by heating ammonium nitrite is also explained in the same way :—

$$\overset{+}{N}\overset{-}{O}_4\overset{+}{H}_4\overset{-}{N} = 4HO + \overset{+}{N}\overset{-}{N}.$$

This mode of regarding the matter is very specially suitable for explaining the reductions by means of hydrogen peroxide, which were at that time partially known and had been chiefly studied by Brodie himself.[8] He regards the formation of oxygen as a consequence of the different polarities which this element possesses in the two oxides. We have, for example :—

$$\overset{+}{H}\overset{-}{O}\overset{+}{O} + \overset{+}{A}g_{\frac{1}{2}}\overset{+}{A}g_{\frac{1}{2}}\overset{-}{O} = HO + \overset{+}{O}\overset{-}{O} + Ag.$$

The reduction of potassium permanganate and of potassium bichromate is supposed to proceed in a similar manner. Two atoms are always set at liberty simultaneously, and these, in consequence of their chemical difference, then unite with each other.[9]

Further, the discovery of ozone by Schönbein ;[10] the recognition of its nature as an isomeric modification of oxygen ;[11] and in particular the proof that it is condensed oxygen (a fact which was first stated by Andrews and Tait[12] on the strength of some highly interesting experiments, but was especially demonstrated by Soret[13]) only find an explanation in the hypothesis of the divisibility of the elementary molecules. If ozone, as appears from Soret's experiments, possesses a relative density, one and a half times as great as that of oxygen, then the smallest particles of this latter gas must contain at least two atoms, whilst those of ozone consist of three atoms. But if this assumption is admitted in the case of oxygen, it cannot easily be avoided in the cases of the other elements. The different vapour densities which were found in the case of sulphur [14] can only be explained by the assumption that, at low temperatures, the molecule consists of three times as many atoms as at a very high temperature.

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[8] Phil. Trans. 1850, 759.

[9] Compare also the explanation which Wurtz gives of the fact that the combination of nitrogen and oxygen takes place much more easily in presence of hydrogen (Wurtz, Leçons. 65).

[10] Pogg. Ann. **50**, 616 ; **59**, 240 ; **63**, 520 ; **65**, 69, 161, 190, etc. ; compare "Ueber das Ozon," Basel 1844.

[11] Archives des sciences phys. et natur., Genève **12**, 315 ; **17**, 61 ; **18**, 153.

[12] Annalen. **104**, 128 ; **112**, 185 ; Ann. Chim. [3] **52**, 333, and **62**, 101.

[13] Annalen. **138**, 45 ; Supplement-band **5**, 148.

The fact is certainly not without interest, that, in 1857, Clausius was led, by the mechanical theory of heat, to the divisibility of the physical molecule.[15] Since, according to this theory, the kinetic energy of translatory motion in equal volumes of two gases at the same pressure, is proportional to the absolute temperature, Clausius concluded that the kinetic energy of translatory motion of the single molecules of all gases at the same temperature is the same. This assumes the fulfilment of Avogadro's hypothesis.

The number of facts drawn from different branches of natural science which tell in favour of this hypothesis might be multiplied still further; but I confine myself to the statement of those that I have mentioned, and pass on to chemical arguments which, after all, were the only ones that eventually led to the recognition of the hypothesis. Amongst these, the experiments which were now carried out and led to the conception of the chemical molecule, distinctly take the first place. I will not assert that this conception was not already extant; but it now appeared in a much more definite form. This latter assertion will certainly be justified when I collect here the facts and hypotheses which existed and exercised an influence upon the determination of molecular weights by chemical methods, prior to Williamson.

The atomic theory gave the first clue to these magnitudes. The formula of every compound required to be expressible by means of multiples, by whole numbers, of the atomic weights; but this had no obligatory consequences so long as the atomic weights had not been determined with certainty, because, in case of necessity, even the atomic weight of a constituent could be altered. It was unquestionable, however, that even with only a moderately consistent application of atomic considerations, there was a certain connection between the different formulæ. A relation of this kind was attained, especially by Laurent and Gerhardt, in the case of organic compounds in particular. It appears to me to follow from the nucleus theory that Laurent assumed the number of carbon atoms in the radical to remain unchanged until carbon was separated in some form or other.[16] It was Gerhardt who first clearly stated this rule[17] (which, however, is not always accurate, as, for example, in the formation of polymeric substances), and it will readily be conceded that by means of it, the molecular weights of many series of compounds were fixed from a knowledge of these magnitudes in the cases of a few substances. The so-called law of the even number of atoms gave a further guide to the smallest formula, and, in consequence of it, Laurent and Gerhardt found frequent occasion to alter the formulæ previously adopted.

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[14] See Dumas: Ann. Chim. [2] **50**, 170, and Deville and Troost, Comptes Rendus. **49**, 239.

[15] Pogg. Ann. **100**, 353.

The conception of the polybasic acids exercised a very important influence in the fixing of formulæ, since even Liebig for example (who first definitely grasped this conception) was induced to double the formula of tartaric acid,[18] in order to make it conform with the chemical character of this substance. In the case of one special class of substances—the acids—the recognition of a criterion of their polybasicity, for which we are indebted to Liebig, Laurent, and Gerhardt, was just as far-reaching as the later experiments of Williamson in the cases of other groups of compounds.

The phenomena of substitution, as may readily be understood, contributed something towards rendering the molecules of different compounds comparable with one another. The formula of a substance frequently required to be multiplied by two or by three so that it might not be necessary to assume fractions of atoms in the products arising from the substance by the action of chlorine, etc. It only became necessary to attend to these considerations in consequence of the unitary notions introduced by Dumas at the same time, and of the rule of Gerhardt mentioned above. This does not apply to the opponents of these views, as I shall prove by means of an example. Kolbe and Frankland prepared methyl (ethan), in 1848, by treating ethyl cyanide with potassium, and they assigned to it the formula C_2H_3 [C=6].[19] They subjected this substance to the action of chlorine in order to convert it eventually into methyl chloride. Instead of the latter they obtained a compound having the same composition as ethyl chloride, but which instead of becoming liquid at 12°, remained gaseous at −18°. This they regarded as isomeric with ethyl chloride, and they formulated it $C_2H_3\,.\,C_2\genfrac{}{}{0pt}{}{H_2}{Cl}$, that is, as a coupled compound of methyl with another atom of methyl in which one atom of hydrogen is replaced by chlorine. With Kolbe and Frankland, therefore, the existence of the first substitution product C_4H_5Cl was no reason for assigning the formula C_4H_6 to the original hydrocarbon. Laurent was of a different opinion. Prior to the isolation of the alcohol radicals, he had proposed for them, in case they should be discovered, the formulæ now adopted.[20] Afterwards, when Kolbe had discovered a general method for the preparation of the alcohol radicals by the electrolysis of salts of the fatty acids,[21] Laurent and Gerhardt return to this view in a detailed manner and designate them as homologues of marsh gas.[22] A. W. Hofmann allies himself with them in so far that he leaves the possibility of isomerism between the alcohol radicals and the homologues of marsh gas an open question.[23] It is otherwise with Frankland, who defends the formulæ corresponding to two volumes for the alcohol radicals, as opposed to those corresponding to four volumes, and formulates methyl, C_2H_3, and ethyl hydride, C_4H_6, afterwards just as he had done before.[24]

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[16] Compare p. 145. [17] J. pr. Chem. **27**, 439. [18] Annalen. **26**, 154.

The conception of the chemical molecule was more readily appreciable by Laurent, Gerhardt, and Hofmann. They endeavoured to make their ideas in this connection plain to their opponents, but still they do not appear to have succeeded in convincing them. Telling experiments were still wanting. Gerhardt required hundreds of examples in order to show that H_4O_2, and not H_2O, corresponds to the formulæ N_2H_6 and H_2Cl_2. Laurent's proof with respect to the doubling of the molecular weights of hydrogen, chlorine, etc., is also clumsy. In spite of this, it cannot be denied that these chemists at that time possessed accurate fundamental ideas, and I do not doubt that they also would have been able to deduce the same conclusions, productive as they were for our science, from the facts which were now discovered and so excellently turned to account by Williamson.

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[19] Journ. Chem. Soc. **1**, 60; Annalen. **65**, 279.

[20] Ann. Chim. [3] **18**, 283.

[21] Journ. Chem. Soc. **2**, 157; A. C. R. **15**, 17; Annalen. **69**, 257.

[22] Comptes rendus mensuels des travaux chimiques, 1850.

[23] Journ. Chem. Soc. **3**, 121; Annalen. **77**, 161.

[24] Journ. Chem. Soc. **3**, 322; Annalen. **77**, 221.

By the action of potassium ethylate upon ethyl iodide, Williamson had hoped to be able to effect the synthesis of an alcohol;[25] ethyl was expected to take the place of the potassium, with the formation of an ethylated ethyl alcohol—an expectation quite in conformity with the views of the period. A short time previously, Wurtz had discovered ethylamine,[26] which he regarded as a substituted ammonia—a view which was confirmed by the interesting mode of formation of this and many analogous substances, discovered by Hofmann.[27] Frankland had already tried by means of zinc ethyl, a substance discovered by himself,[28] to introduce alcohol radicals into organic substances.[29] But Williamson's experiment gave unexpected results: instead of an alcohol, he obtained ether. He understands, however, how to adapt his ideas, which had been turned in an altogether different direction, to his results, and he at once recognises the full importance of his experiment. He explains the formation of ether under the conditions which he had observed, and then the formation of ether in general; and he proves the accuracy of his view by means of a series of brilliant experiments.

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[25] Phil. Mag. [3] **37**, 350; A. C. R. **16**, 7, 8; Annalen. **77**, 37.

[26] Comptes Rendus. **28**, 223.

[27] Journ. Chem. Soc. **1**, 159, etc.; Annalen. **66**, 129, etc.

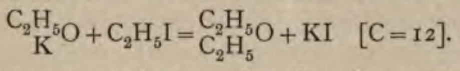
[28] Journ. Chem. Soc. **2**, 297; Phil. Trans. 1852, 417; Annalen. **71**, 213; **85**, 329.

[29] Phil. Trans. 1852, 432.

Different views were at that time held as to the formulæ of alcohol and of ether. In conformity with Liebig's ethyl theory, alcohol was pretty generally written $C_4H_{12}O_2$, and ether $C_4H_{10}O$ [$C=12, O=16$]. Now, with the halving of the atomic weights, the formulæ had, in many cases, been halved: alcohol became $C_4H_6O_2$, and ether C_4H_5O [$C=6, O=8$], whereas Gerhardt assigned to these substances the formulæ C_2H_6O and $C_4H_{10}O$ [$C=12, O=16$]. Further, Laurent had already drawn attention to the fact, in 1846,[30] that the formulæ of alcohol and ether, as well as those of potassium oxide and hydroxide, are derivable from that of water.[31] He wrote :—

HHO	EtHO	EtEtO	KHO	KKO
Water.	Alcohol.	Ether.	Potassium Hydroxide.	Potassium Oxide.

Williamson perceived that the last view alone was in agreement with his experiment. He formulated as follows the equation which represented the reaction he had discovered :—



$$\begin{matrix}C_2H_5\\K\end{matrix}O + C_2H_5I = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}O + KI \quad [C=12].$$

In order to meet the opposing view, in accordance with which the equation ought to be written :—

$$C_4H_5O\,.\,KO + C_4H_5I = 2(C_4H_5O) + KI \quad [C=6]$$

since the assumption was that potassium alcoholate is a compound of potassium oxide with ether, and that the latter separated during the decomposition, whilst a second "atom" of the same substance was simultaneously produced from the ethyl iodide, Williamson carried out the reaction with methyl iodide. He expected to obtain methyl ethyl ether, whereas, in accordance with the view just referred to, a mixture of methyl ether and ethyl ether ought to be produced. The experiment was, therefore, decisive and justified Williamson's hypothesis. Both by the action of methyl iodide upon potassium ethylate and by that of ethyl iodide upon potassium methylate the so-called mixed methyl ethyl ether was produced :—

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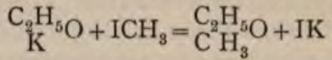
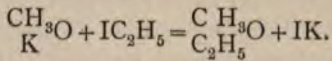
[30] Ann. Chim. [3] 18, 266.

[31] Griffin claims priority with respect to the view that the alkalies do not contain any water. See Griffin, Radical Theory, 9.



$$\substack{C_2H_5\\K}O + ICH_3 = \substack{C_2H_5\\C\,H_3}O + IK$$



$$\substack{CH_3\\K}O + IC_2H_5 = \substack{C\,H_3\\C_2H_5}O + IK.$$

These experiments proved to Williamson that ether is produced from alcohol by the replacement of an atom of hydrogen by ethyl, and, therefore, that it contains more carbon in its molecule than alcohol does. The formation of the mixed ethers furnished him with a reason for excluding every other view.

It now became a question to explain the formation of ether under known circumstances, especially by the treatment of alcohol with sulphuric acid ; and the solution of this problem was also furnished by Williamson, after chemists had been engaged upon it for decades. At first the process of etherification had been explained by the dehydrating action of sulphuric acid.[32] This view agreed very well with Dumas' etherin theory. Hennell, although an adherent of the etherin theory, considered this view irreconcilable with the formation of sulphovinic acid observed by him ;[33] and it was also in contradiction with the fact that water distils over at the same time as the ether. It was Liebig, especially, who established by means of numerous experiments a new theory of etherification.[34] He ascertained that the formation of ethyl sulphuric acid precedes that of ether, and, according to him, the sulphuric acid does not withdraw water from the alcohol, but ether, which latter unites with the sulphuric acid. Indeed ethyl sulphuric acid was at that time looked upon as a compound of these two substances, that is, as an acid salt of ethyl oxide.

$$\text{Thus ethyl sulphuric acid} = C_4H_{10}O + 2SO_3 + H_2O$$
$$[C = 12,\ O = 16,\ S = 32].$$

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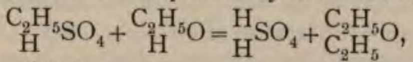
[32] Compare especially Fourcroy and Vauquelin, Scherer's Journal **6**, 436 ; also Gay-Lussac, Ann. Chim. **95**, 311, and [2] **2**, 98. [33] Phil. Trans. 1828, 369. [34] Annalen. **9**, 31 ; **13**, 27 ; **23**, 31.

Ethyl sulphuric acid, according to the experiments of Liebig, breaks up between 127° and 140° into ether and sulphuric acid. The remarkable phenomenon that a substance is produced and undergoes decomposition in the same operation, was explained by Liebig on the assumption that the formation only occurred at those places where the alcohol dropped in, and where, therefore, the temperature was lowered to the boiling point of this liquid. The process of etherification therefore consisted, according to Liebig, in the combination of the sulphuric acid with the ether of the alcohol, and the decomposition into its constituents of the compound so formed, at parts of the liquid where the temperature was higher. Ether then distils over, and, along with it, the water which was separated on the formation of the ethyl sulphuric acid.

In opposition to this theory Berzelius[35] advanced another view, which was supported and developed by Mitscherlich in particular.[36] According to this view, the sulphuric acid acts by contact, taking no part in the reaction, and simply decomposing the alcohol into ether and water by catalytic action. This was a mode of expressing the facts by means of specially chosen words, but it can scarcely be called an explanation. Liebig's hypothesis really embraced an explanation which was pretty generally accepted. It was only called in question after Graham had shown, in 1850,[37] that alcohol and ethyl sulphuric acid are both necessary for the formation of ether; and that the latter of the two does not yield ether even when heated alone to 143°, but decomposes, in presence of water, into alcohol and sulphuric acid.

Williamson clearly understands how to apply these facts. The formation of ether is explained by the following equation:



$$\begin{matrix}C_2H_5\\H\end{matrix}SO_4+\begin{matrix}C_2H_5\\H\end{matrix}O=\begin{matrix}H\\H\end{matrix}SO_4+\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O,$$

Ethyl sulphuric acid.	Alcohol.	Sulphuric acid.	Ether.

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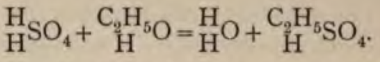
[35] Berzelius, Jahresbericht, 1836, 241.

[36] Pogg. Ann. 53, 95; 55, 209.

[37] Journ. Chem. Soc. 3, 24; Annalen. 75, 108; compare Journ. de pharm. [3] 18, 30.

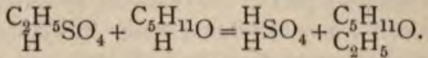
whilst the formation of the ethyl sulphuric acid is represented by this one :—



$$\begin{matrix}H\\H\end{matrix}SO_4 + \begin{matrix}C_2H_5\\H\end{matrix}O = \begin{matrix}H\\H\end{matrix}O + \begin{matrix}C_2H_5\\H\end{matrix}SO_4.$$

If the latter equation is read from right to left, it explains Graham's experiment of the decomposition of ethyl sulphuric acid into alcohol and sulphuric acid. As soon as the doubled formula for ether was admitted, it was comprehensible why ether is not produced by heating ethyl sulphuric acid.

Williamson, however, not contented with having shown the accuracy of his opinions by their being in harmony with the known facts, devises new experiments by which he can test them.[38] The method he adopts is the same as previously. He chooses the two substances which act upon one another from groups containing different numbers of carbon atoms. He now causes ethyl sulphuric acid and amyl alcohol to interact, and this reaction gives rise to the expected ethyl amyl ether :—



$$\begin{matrix}C_2H_5\\H\end{matrix}SO_4 + \begin{matrix}C_5H_{11}\\H\end{matrix}O = \begin{matrix}H\\H\end{matrix}SO_4 + \begin{matrix}C_5H_{11}\\C_2H_5\end{matrix}O.$$

He studies, besides, the action of sulphuric acid upon mixtures of ethyl and amyl alcohols, and is able to show the formation, in this case, of three ethers—ethyl ether, amyl ether, and ethyl amyl ether. He finds "in these reactions the best evidence of the nature of the action of sulphuric acid in forming common ether, or in accelerating the formation of the so-called compound ethers; for acetic ether is formed from acetic acid, just as ethylic ether from alcohol, by the replacement of hydrogen by ethyle. And if the circumstance of containing hydrogen, which is replaceable by other metals or radicals, be the definition of an acid, we must consider alcohol as acting the part of an acid in these reactions."

A further consequence of Williamson's experiments was the fixing of the molecular weight of acetic acid. According to Williamson, this acid is formed from alcohol by the replacement of two hydrogen atoms of the ethyl group by an atom of oxygen, the radical C_2H_5, ethyl, being converted by oxidation into C_2H_3O, othyl. Acetic acid is now regarded as water in which one atom of hydrogen is replaced by othyl. The formula $C_6H_{12}O_3$ fixed upon for acetone by Kane,[39] did not appear to be in harmony with this; it had, however, already been halved, and Williamson endeavoured to explain the formation of the substance during the distillation of the acetates, by means of the following equation:—

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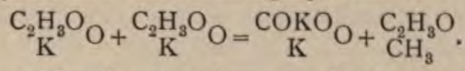
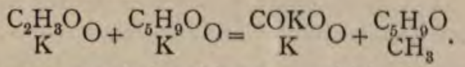
[38] Journ. Chem. Soc. **4**, 229; A. C. R. **16**, 24; Annalen. **81**, 73.



$$\begin{matrix}C_2H_3O\\K\end{matrix}O+\begin{matrix}C_2H_3O\\K\end{matrix}O=\begin{matrix}COKO\\K\end{matrix}O+\begin{matrix}C_2H_3O\\CH_3\end{matrix}.$$

According to him, the potassium peroxide is replaced during the reaction by methyl derived from the othyl. Here, also, he checks his opinion by applying the method already mentioned. He distils mixtures of acetates and valerianates and obtains mixed ketones:—



$$\begin{matrix}C_2H_3O\\K\end{matrix}O+\begin{matrix}C_5H_9O\\K\end{matrix}O=\begin{matrix}COKO\\K\end{matrix}O+\begin{matrix}C_5H_9O\\CH_3\end{matrix}.$$

Williamson concludes this paper, which did a great deal to advance chemistry, with the words: "The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of."

The "*terme de comparaison*" which Laurent had already sought for in vain, had now been found. Substances were to be conceived as formed from water in accordance with the proposal, which Williamson makes in 1851 in his famous paper upon salts,[40] to regard this substance as the type for all compounds. His method of fixing molecular weights is a purely chemical one; he regards compounds as formed from water by the replacement of one or of two atoms of hydrogen. Inasmuch as he tests all his views by means of facts already known, as well as by means of new experiments, these views obtain, I might almost say, absolute confirmation. His experiments, moreover, are not chosen at random, but are always suggested by the same kind of logical deductions. Williamson furnished thinking chemists with the means of determining molecular weights by chemical methods. The very general applicability of the method which he discovered, is demonstrated by the fine experiments of Gerhardt, who was led by it to the preparation of the mixed anhydrides,[41] and of Wurtz, who employed it with similar success in fixing the formulæ of the alcohol radicals.[42] The mode, also, in which Friedel and Crafts[43] determined the molecular weight of silicic ether depends upon a train of ideas that only became clear to chemists after the publication of Williamson's investigations.

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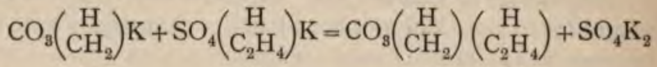
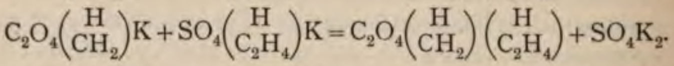
[39] Annalen. **22**, 278. [40] Journ. Chem. Soc. 4, 350; A. C. R. **16**, 41.

The fact must not remain unmentioned here that, only a few months after Williamson's publication, Chancel, on 7th October 1850, published a paper[44] in which, by means of similar experiments, he arrived at the same results as Williamson. Chancel distils potassium ethyl sulphate with potassium ethylate, and with potassium methylate, and thus obtains ethyl ether and ethyl methyl ether. His mode of fixing the molecular weight of dibasic acids is peculiar to himself, although it coincides, in principle, with Williamson's method. By distilling potassium ethyl sulphate with potassium methyl carbonate and with potassium methyl oxalate, Chancel prepares ethyl methyl carbonate and ethyl methyl oxalate. The reactions are represented by the following equations:—



$$CO_3\binom{H}{CH_2}K + SO_4\binom{H}{C_2H_4}K = CO_3\binom{H}{CH_2}\binom{H}{C_2H_4} + SO_4K_2$$



$$C_2O_4\binom{H}{CH_2}K + SO_4\binom{H}{C_2H_4}K = C_2O_4\binom{H}{CH_2}\binom{H}{C_2H_4} + SO_4K_2.$$

The experiments of Williamson and of Chancel were of the greatest importance in the development of the science, for our present views are founded upon the conception of the chemical molecule. Unfortunately it is not always possible to determine this with the same exactness as in the cases considered above. It became manifest, however, that with few exceptions, to which we shall afterwards return, the chemical molecule agrees with the molecular weight deduced from the observed volume, on the basis of Avogadro's hypothesis. This led to the assumption of the general identity of the physical and the chemical molecule, whereby a new means, and an almost always sufficient one, is furnished for ascertaining the highly important molecular weight.

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[41] Ann. Chim. [3] **37**, 332; Annalen. **82**, 127; **83**, 112; **87**, 57 and 149.

[42] Ibid. **96**, 364.

[43] Ann. Chim. [4] **9**, 5.

[44] Comptes Rendus. **31**, 521.

But Williamson's experiments and opinions also exerted an influence in another direction; that is, with respect to the views concerning the constitution of compounds. The way was now prepared for a fusion of the newer radical theory or theory of residues with Dumas' theory of types, from which Gerhardt's theory of types arose. In this development the labours of other chemists were, however, of at least as great importance, especially as these had already been partially carried out. Accordingly, we shall now direct our attention more particularly to the latter.

In 1849, Wurtz, by treating cyanic ether, cyanuric ether, and the substituted ureas prepared from these by himself, with potash, obtained bases extremely like ammonia, which he compared with the latter inasmuch as he regarded them as ammonia in which an atom of hydrogen is replaced by a radical such as methyl, ethyl, amyl, etc.[45] This way of regarding these substances involved an important step in advance, since it was the first successful attempt to introduce radicals into the types.[46] The fact that Liebig, as early as 1839, expressed a similar view concerning these substances, which were then only hypothetical,[47] satisfactorily proves the clear perception of this gifted scientist, but cannot detract from the merit of Wurtz.

The views of Wurtz respecting the constitution of these artificial bases, received important support from Hofmann's method of preparing them.[48] Hofmann succeeded, by treating the alkyl iodides with ammonia, in introducing the radicals into the latter, and his experiments possess all the greater importance from the fact that he also showed how to prepare secondary and tertiary compounds, as well as substances corresponding to ammonium chloride and ammonium hydroxide.

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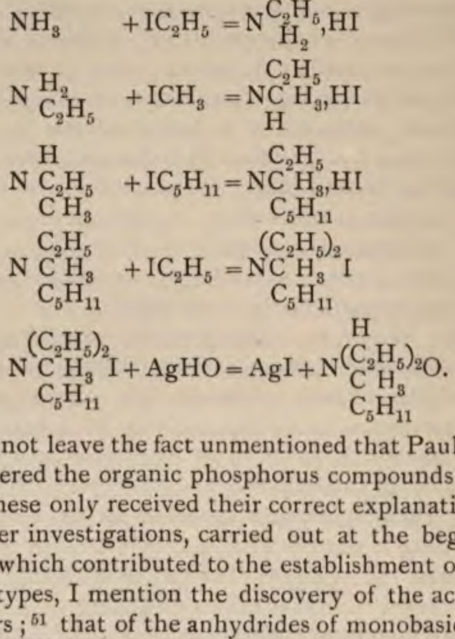
[45] Comptes Rendus. **28**, 224, 323; **29**, 169, 186; Annalen. **71**, 330.

[46] Compare, however, Laurent, Ann. Chim. [3] **18**, 266.

[47] Handwörterbuch der Chemie, by Liebig, Poggendorff, and Wöhler, **1**, 698.

Thus :



$$NH_3 + IC_2H_5 = N\begin{matrix}C_2H_5\\H_2\end{matrix},HI$$

$$N\begin{matrix}H_2\\C_2H_5\end{matrix} + ICH_3 = N\begin{matrix}C_2H_5\\CH_3\\H\end{matrix},HI$$

$$N\begin{matrix}H\\C_2H_5\\CH_3\end{matrix} + IC_5H_{11} = N\begin{matrix}C_2H_5\\CH_3\\C_5H_{11}\end{matrix},HI$$

$$N\begin{matrix}C_2H_5\\CH_3\\C_5H_{11}\end{matrix} + IC_2H_5 = N\begin{matrix}(C_2H_5)_2\\CH_3\\C_5H_{11}\end{matrix}I$$

$$N\begin{matrix}(C_2H_5)_2\\CH_3\\C_5H_{11}\end{matrix}I + AgHO = AgI + N\begin{matrix}H\\(C_2H_5)_2\\CH_3\\C_5H_{11}\end{matrix}O.$$

I shall not leave the fact unmentioned that Paul Thenard had discovered the organic phosphorus compounds in 1845,[49] but that these only received their correct explanation now.[50]

Of other investigations, carried out at the beginning of the fifties, which contributed to the establishment of the new theory of types, I mention the discovery of the acichlorides by Cahours ;[51] that of the anhydrides of monobasic acids by Gerhardt ; Williamson's researches on dibasic acids ; and, finally, the preparation of the acid amides of Gerhardt and Chiozza.[52]

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[48] Annalen. **66**, 129 ; **67**, 61, 129 ; **70**, 129 ; **73**, 180 ; **74**, 1, 33, 117 ; **75**, 356 ; **78**, 253 ; **79**, 11.

[49] Comptes Rendus. **21**, 144 ; **25**, 892.

[50] Compare Frankland, Annalen. **71**, 215.

[51] Ibid. **70**, 39. Liebig and Wöhler had prepared benzoyl chloride and benzoyl-amide twenty years before ; see Annalen. **3**, 249.

[52] Comptes Rendus. **37**, 86.

Gerhardt had at once grasped the bearings of Williamson's investigations, and was only able to perceive in them confirmation of the views already upheld, at an earlier date, by himself and Laurent but never stated with the same precision.[53] He perceived that Williamson's reaction for the formation of ether might also be applied to the monobasic acids, and that the oxides or anhydrides of the latter should be obtained in this way.[54] The experiment succeeded, and thus it was reserved for Gerhardt, who, as well as Laurent, had denied the existence of anhydrides of monobasic acids, to disprove this view by his own experiments. He had, it is true, previously only stated the impossibility of withdrawing a molecule of water from one molecule of acid, and this statement still held; for he showed that two molecules of a monobasic acid are always concerned in the formation of the anhydride, and the proof was furnished by Williamson's method. By treatment of potassium acetate with acetyl chloride, Gerhardt obtained acetic anhydride :—

$$\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O + C_2H_3OCl = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + KCl,$$

and by employing benzoyl chloride he obtained the intermediate anhydride of benzoic and of acetic acids :—

$$\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O + C_7H_5OCl = \left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O + KCl.$$

Before turning to the researches carried out jointly by Gerhardt and Chiozza on the anhydrides and amides of dibasic acids, I must give an account of the conception which Williamson introduced concerning these acids, whereby the stimulus was given that led to these researches. The extension which Williamson gave in 1851 (that is, a year after his first investigation on etherification) to the views already arrived at, was an extremely important one. Even if it may perhaps be said that in his previous publications he leaned towards the views of Laurent and Gerhardt, and merely confirmed these by means of new, although certainly most decisive, experiments, he now appears in a perfectly independent and original manner.

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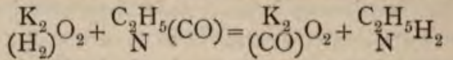
[53] See his claim: Annalen. **91**, 198.

[54] Ann. Chim. [3] **37**, 332.

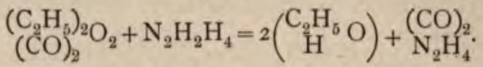
Williamson shows how the existence of dibasic acids depends upon the presence of radicals with basicity greater than one.[55] The formation of the substituted ammonias, in the reaction discovered by Wurtz, which he formulates :—



$$\begin{matrix}K_2\\(H_2)\end{matrix}O_2+\begin{matrix}C_2H_5\\N\end{matrix}(CO)=\begin{matrix}K_2\\(CO)\end{matrix}O_2+\begin{matrix}C_2H_5\\N\end{matrix}H_2$$

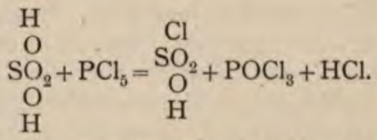
gives him occasion to express himself as follows :—"One atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, holds together the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\begin{matrix}(CO)\\K_2\end{matrix}O_2$, carbonate of potash."

By further assuming that carbonic oxide can double its atomic weight, without alteration of its basicity (or equivalence), he obtains in C_2O_2 the radical of oxalic acid, and is able to represent the formation of oxamide by means of the equation :—



$$\begin{matrix}(C_2H_5)_2\\(CO)_2\end{matrix}O_2+N_2H_2H_4=2\left(\begin{matrix}C_2H_5\\H\end{matrix}O\right)+\begin{matrix}(CO)_2\\N_2H_4\end{matrix}.$$

The conception of sulphuric acid as a dibasic hydrate of the radical SO_2 is highly important, and the experiments which Williamson carries out in support of this view are most interesting. Besides the known chloride SO_2Cl_2, which Regnault had prepared from sulphurous anhydride and chlorine,[56] he succeeds in isolating also chlorosulphonic acid, by treating sulphuric acid with phosphorus pentachloride.[57] Thus :



$$\begin{matrix}H\\O\\SO_2\\O\\H\end{matrix}+PCl_5=\begin{matrix}Cl\\SO_2\\O\\H\end{matrix}+POCl_3+HCl.$$

By means of this experiment he disproves the view of Gerhardt, in accordance with which the formation of the anhydride is always supposed to precede that of the chloride in the case of dibasic acids.[58] Thus Gerhardt, conjointly with Chiozza, had published, in June 1853 (and thus half a year before this last paper of Williamson's appeared), investigations on the derivatives of dibasic acids, and especially on their anhydrides and chlorides, in which he thought it was shown, amongst other things, that the first action of phosphorus pentachloride consists in the removal of water, and that it is only in the second stage of the reaction that a substance containing chlorine is produced. Gerhardt and Chiozza arrived at this time, however, at very important results; they regarded the dibasic anhydrides, for the first time, as water in which both the hydrogen atoms are replaced by a single radical, and they also showed how to prepare succinyl chloride and similar chlorides. In two subsequent papers[59] they deal with the investigation of the amides corresponding to the polybasic acids. They show that these are either derived from two molecules of ammonia which are held together by the replacement, by a dibasic radical, of one atom of hydrogen in each, or that they may be derived from one molecule of ammonia. The amid-acids correspond to the mixed type NH_3+H_2O, which can only be produced by the polyatomic acid radical entering the molecule; and the earlier statement of Gerhardt that only dibasic acids could give rise to the formation of amid-acids is thus explained.

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[55] Journ. Chem. Soc. **4**, 350. [56] Ann. Chim. [2] **69**, 170; **71**, 445.

[57] Proc. Roy. Soc. **7**, 11; Annalen. **92**, 242.

By these and similar experiments, but especially by adopting the ingenious conclusions that Williamson had drawn from his investigations, Gerhardt is able to establish a complete classification of organic compounds according to a new principle,[60] and he expounds this classification in the fourth volume of his excellent Hand-book.

An important point in Gerhardt's system consists in his showing the connection between substances of opposite character by means of intermediate substances.

Unlike the dualists, he does not contrast such substances as potash and sulphuric acid as absolutely opposite in character, but he connects them by means of transition compounds, and thus obtains series in which he arranges substances. In arranging these series he makes use of two generalisations, of which, however, one does not originate with himself. In 1842, Schiel had pointed out[61] that the alcohol radicals form a series whose separate members differ by $n.CH_2$, and that the corresponding alcohols show a difference in boiling point of 18° for each CH_2, as Kopp had already proved in the case of ethyl and methyl compounds.[62] In 1843, Dumas showed[63] that the fatty acids also possess, amongst themselves, the same difference in composition. Gerhardt now employs this very striking regularity, which, as is well known, occurs amongst very many organic substances, and calls the compounds which differ by $n.CH_2$, homologous. It had been found that such compounds possess great similarities to one another, and that their physical properties slowly and progressively change. This had especially appeared from Kopp's detailed and excellent investigations.[64] Gerhardt establishes, further, the idea of isologous compounds: these substances are also chemically similar but their difference in composition is not $n.CH_2$. Acetic and benzoic acids are well-known examples belonging to this class of substances.

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[58] Comptes Rendus. 36, 1050. [59] Ibid. 37, 86; 38, 457. [60] Gerhardt, Traité de Chimie organique, 4, quatrième partie.

The homologous and isologous series constitute the one part of Gerhardt's classification; the other part is represented by the heterologous series. All substances are referred to the latter which can be obtained from one another by means of simple reactions (by double exchange); these substances are allied in their mode of formation but they are chemically different. Gerhardt very appropriately regards this arrangement of the compounds as similar to a game of cards which is based upon the colour as well as upon the value of the separate cards. Just as in the latter every card which is wanting is characterised by its vacant place, as of a certain value and of a certain colour, so the chief properties, the formation, and the decomposition of the terms which are wanting in the chemical classification can be stated beforehand.

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[61] Annalen. **43**, 107. [62] Ibid. **41**, 79. [63] Ibid. **45**, 330. [64] Ibid. **41**, 169; **50**, 71; **55**, 166; **64**, 212; **92**, 1; **94**, 257; **95**, 121, 307; **96**, 1, 153, 303; **98**, 367; **100**, 19, etc.

Gerhardt compares the members of one and the same heterologous series (representative, therefore, of the various homologous and isologous series) with four very minutely studied inorganic substances, as prototypes, viz., water, hydrochloric acid, hydrogen, and ammonia—all compounds of hydrogen. A substance which was to be regarded as belonging to one of these types, was necessarily capable of being conceived as derived from it by the replacement of hydrogen atoms by radicals. Thus Gerhardt refers alcohols, ethers, acids, anhydrides, salts, aldehydes, ketones, etc., to the water type, and to this type there also belong the mercaptans, sulphides, etc. The latter really correspond to the type of sulphuretted hydrogen, but this is merely a subdivision of the water type. Chlorides, bromides, iodides, and cyanides are referred to hydrochloric acid. Ammonia was the prototype of the amines, amides, imides, and nitriles, as well as of the corresponding phosphorus compounds. Finally, the hydrocarbons, the alcohol radicals and the radicals containing metals were referred to the hydrogen type, H_2.

The great step had, accordingly, now been taken ; radicals had been introduced into the mechanical types of Regnault and of Dumas. If we look back and inquire to whom we are chiefly indebted for this excellent extension of the earlier theory of types, the names of Laurent and of Wurtz especially deserve to be mentioned. As early as 1846, the former had referred alcohol and ether to water ; three years later, Wurtz discovered ethylamine which he regarded as a substituted ammonia. This view met with acceptance all the more rapidly that the similarity between the two substances is so startling.[65] I shall not omit to observe here again, that the conception of the radical was now adopted in the sense in which Gerhardt had defined it in 1839. Radicals were residues of compounds, *i.e.*, they were atomic groups which, in certain reactions, could be transferred, undecomposed, from one substance to another; they did not, however, on this account at all require to exist independently, and they were only intended to express the relation in which elements or atomic groups are replaced.[66]

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[65] With respect to the share which Hunt took in the development of the theory of types, compare Silliman's Journal [2] **5**, 265 ; **6**, 173 ; **8**, 92 ; **9**, 65 ; also Phil. Mag. [4] **3**, 392. His claim is printed in Comptes Rendus. **52**, 247, and the reply of Wurtz in Répert. de Chimie pure. **3**, 418.

The formulæ which are thus obtained for compounds, do not indicate the arrangement of the atoms; they are merely reaction formulæ, which recall a series of analogies. It can thus be understood how Gerhardt could imagine several radicals and several rational formulæ in the case of the same substance. The determination of the true constitution of substances appeared to him a task not capable of accomplishment, since modes of formation and of decomposition can alone lead to a judgment respecting it, and the multiplicity of these does not permit of any conclusion as to the arrangement of the atoms. Thus, for example, barium sulphate is formed from sulphuric acid and baryta, from sulphurous acid and barium peroxide, and besides, from barium sulphide and oxygen. The constitution of the salt might, therefore, be represented symbolically by means of the three formulæ:—

$$Ba_2O + SO_3, \quad Ba_2O_2 + SO_2, \quad Ba_2S + O_4$$ [67]

$$(O = 16, S = 32, Ba = 68.5).$$

By means of this single example Gerhardt considered himself able to prove that all endeavours directed towards the representation of the arrangement of the atoms by means of symbols, must lead to nothing.

With Gerhardt, reactions are double decompositions; and here the contrast is seen between his system and the dualistic system, in which all compounds are conceived as formed by additions. Gerhardt goes so far as even to assume a double decomposition, or as he calls it, a typical reaction, when two molecules unite to form a single one. Thus ethylene chloride, according to him, is produced from olefiant gas in consequence of the substituting action of chlorine. The chloride C_2H_3Cl

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[66] Gerhardt, Traité de Chimie organique. 4, 569. [67] Compare p. 177.

is formed, and this remains united with the hydrochloric acid which is produced simultaneously.[68]

The general arrangement and the comprehensive character of Gerhardt's system leave nothing to be desired. Even although our views have been considerably changed and cleared up since that time, and although we are compelled, from our present standpoint, to look upon the types as insufficient, still Gerhardt's services to chemistry can never be questioned. Unfortunately he was not long able to congratulate himself on the acceptance that his admirable Hand-book met with, as he died shortly after its completion.

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[68] Compare p. 149.

LECTURE XII.

MIXED TYPES—RELATION BETWEEN KOLBE'S VIEWS AND THE COPULÆ OF BERZELIUS — RADICALS CONTAINING METALS — CONJUGATED RADICALS—KOLBE AND FRANKLAND AND THE VIEWS REGARDING TYPES—POLYBASICITY AS AN EVIDENCE FOR THE ACCURACY OF THE NEW ATOMIC WEIGHTS — DISCOVERY OF THE POLYATOMIC ALCOHOLS AND AMMONIAS.

I AGAIN desire to direct attention to the theory of types in the form in which it had been established by Gerhardt. The latter had divided organic substances into natural families, if I may so express myself, represented by the four types, water, hydrochloric acid, ammonia, and hydrogen, which were also called by him types of double decomposition. In this connection it must be pointed out that Gerhardt assumes the existence of conjugated radicals, so as to be able to include substitution products also in the types, and "to connect with one another several systems of double decomposition of a substance."[1] For this purpose he employed, in part at least, the same mode of regarding substances as Kolbe, an exposition of which I have still to give.

It must now be pointed out that the conjugated compounds are no longer considered in the sense previously stated by Gerhardt; and not only has the name of the "corps copulés" been changed into "corps conjugés," but the signification of the thing itself has been altered. The law of basicity, already discussed in detail, no longer finds any application;[2] monobasic acids can now give rise to conjugated compounds by interacting with neutral substances; and to this class of conjugated compounds there are now reckoned all the substances produced by substitution (acids especially), and consequently the substances obtained by the action of chlorine, bromine, iodine, nitric acid, sulphuric acid, etc., upon organic materials. Accordingly, the conjugated radicals were, as we should now say, substituted radicals, and they embraced, besides, the atomic groups containing a metal, such as cacodyl, etc.

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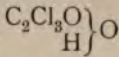
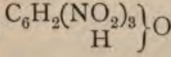
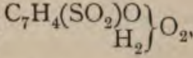
[1] Gerhardt, Traité. 4, 604.

[2] Compare p. 183.

Whilst Gerhardt placed chloracetic acid  $\left.\begin{matrix}C_2Cl_3O\\ H\end{matrix}\right\}O$, picric acid  $\left.\begin{matrix}C_6H_2(NO_2)_3\\ H\end{matrix}\right\}O$, sulphobenzoic acid  $\left.\begin{matrix}C_7H_4(SO_2)O\\ H_2\end{matrix}\right\}O_2$, etc. in this class of substances, other chemists, Mendius for example,[3] only cared to call substances of the latter kind conjugated; whereas others still, such as Limpricht and Uslar,[4] would have wished to see almost all organic compounds placed in this category. A discussion took place in connection with this subject which ended with the introduction of the mixed types and the abandonment of the conjugated compounds.

Gerhardt had already referred the amid-acids, which he places in his text-book amongst the "acides conjugés," to the type ammonia + water[5] in 1853. Returning to this idea, but, at the same time giving it an important extension, Kekulé shows, in 1857, upon the assumption of mixed types, how a distinction between conjugated and other compounds becomes quite unnecessary.[6] The possibility of this hypothesis rested upon the conception of the polybasic radicals introduced in 1851 by Williamson, and by means of this conception it became comprehensible how two molecules, previously separate, may be united into a single one. Williamson had explained the joining together of two molecules of water as depending upon the nature of the radical SO_2, and in this way the condensed types arose. Kekulé employs this view in establishing the mixed types. With respect to this he expresses himself as follows:—" A union of several molecules of the types can only occur when, by the entrance of a polyatomic radical in place of two or three atoms of hydrogen, a cause is furnished for the holding of these molecules together." Since an unlimited number of heterogeneous molecules may unite in this manner, even the most complicated compounds could be referred to types. There was thus no longer any necessity to have recourse to conjugated compounds, and Kekulé further points this out:—"The so-called conjugated compounds are not composed in any manner different from other compounds; they can be referred in the same manner to types in which hydrogen is replaced by radicals; they follow the same laws with respect to their formation and saturating capabilities as hold for all chemical compounds."

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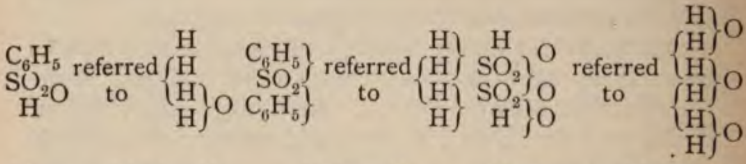
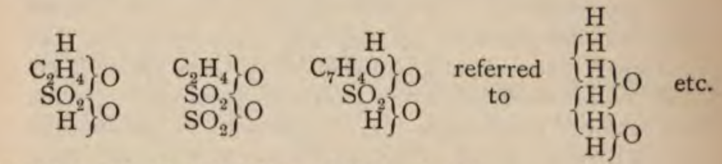
[3] Annalen. 103, 39.
[4] Ibid. 102, 239.
[5] Compare p. 215.
[6] Annalen. 104, 129.

With a view to facilitating a better comprehension of Kekulé's ideas, I give below a few of the formulæ proposed by him:—



$$\begin{array}{c} C_6H_5 \\ SO_2O \\ H \end{array} \text{ referred to } \begin{array}{l} H \\ \left\{\begin{array}{l} H \\ \left.\begin{array}{l} H \\ H \end{array}\right\}O \end{array}\right. \end{array} \qquad \left.\begin{array}{c} C_6H_5 \\ SO_2 \\ C_6H_5 \end{array}\right\} \text{ referred to } \begin{array}{c} \left.\begin{array}{c} H \\ H \end{array}\right\} \\ \left.\begin{array}{c} H \\ H \end{array}\right\} \end{array} \begin{array}{l} \left.\begin{array}{c} H \\ SO_2 \end{array}\right\}O \\ \left.\begin{array}{c} SO_2 \\ H \end{array}\right\}O \end{array} \qquad \text{ referred to } \begin{array}{l} \left.\begin{array}{c} H \\ H \end{array}\right\}O \\ \left.\begin{array}{c} H \\ H \end{array}\right\}O \\ \left.\begin{array}{c} H \\ H \end{array}\right\}O \end{array}$$

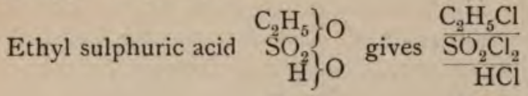
Benzene sulphonic acid. Sulfobenzide. Nordhausen sulphuric acid.



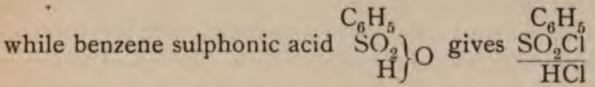
$$\begin{array}{l} H \\ \left.\begin{array}{c} C_2H_4 \\ SO_2 \end{array}\right\}O \\ \left.\begin{array}{c} SO_2 \\ H \end{array}\right\}O \end{array} \qquad \begin{array}{l} \left.\begin{array}{c} C_2H_4 \\ SO_2 \end{array}\right\}O \\ \left.\begin{array}{c} SO_2 \\ SO_2 \end{array}\right\}O \end{array} \qquad \begin{array}{l} H \\ \left.\begin{array}{c} C_7H_4O \\ SO_2 \end{array}\right\}O \\ \left.\begin{array}{c} SO_2 \\ H \end{array}\right\}O \end{array} \text{ referred to } \begin{array}{l} H \\ \left\{\begin{array}{l} H \\ \left.\begin{array}{l} H \\ H \end{array}\right\}O \\ \left.\begin{array}{l} H \\ H \end{array}\right\}O \end{array}\right. \end{array} \text{ etc.}$$

Isethionic acid. Carbyl-sulphate. Sulfobenzoic acid.

The way in which Kekulé employs the reaction with pentachloride of phosphorus, in order to distinguish from each other the types H_2 and H_2O, is interesting, and I shall mention it here in passing. Kekulé points out how the oxygen in water is replaced, by means of this reagent, by two atoms of chlorine, whereby the molecules corresponding to this type are broken up, whilst those deducible from the hydrogen type are preserved :—



$$\text{Ethyl sulphuric acid} \quad \begin{array}{r} C_2H_5 \\ SO_2 \\ H \end{array}\begin{array}{l} \}O \\ \\ \}O \end{array} \quad \text{gives} \quad \begin{array}{c} C_2H_5Cl \\ \hline SO_2Cl_2 \\ \hline HCl \end{array}$$



$$\text{while benzene sulphonic acid} \quad \begin{array}{r} C_6H_5 \\ \left.\begin{array}{r} SO_2 \\ H \end{array}\right\}O \end{array} \quad \text{gives} \quad \begin{array}{c} C_6H_5 \\ SO_2Cl \\ \hline HCl \end{array}$$

It was by means of the theory of mixed types (the last consequence of this mode of regarding substances) that Gerhardt's system first attained that uniform character in which it dominated organic chemistry for several years. But after the idea of the types had been recognised,[7] they themselves became unnecessary. The theory of types was only a formal conception, which lost its importance as soon as its real teaching had been grasped. It had been necessary, however, for the origination of the views as to atomicity then in process of development. Particularly active in this connection were Williamson, Wurtz, Odling, and especially Kekulé—that is to say, the chemists who had already taken an important part in establishing the theory of types. Simultaneously, however, such important services were rendered, from an altogether different side (that is, from the opponents of Gerhardt and successors of Berzelius), both by means of theoretical speculations and of experimental investigation, that before we turn to the theory of atomicity and the views arising from it as to the mutual relations of the atoms, we shall look more closely at the labours of that school which had sprung up from the ruins of the system of Berzelius.

In doing so, I may be permitted to go a long way back and state the facts which, in my opinion, led from the copulæ of Berzelius to the important views of Kolbe.

Magnus has shown, at the beginning of the fourth decade of the nineteenth century,[8] that the salts of ethyl sulphuric acid, dried *in vacuo* over sulphuric acid, correspond to the old formula of Serullas,[9] $C_4H_8 + 2SO_3 + MO + H_2O$ [$C = 12, S = 32, O = 16$]. Liebig confirmed this,[10] and was thereby led to pronounce ethyl sulphuric acid isomeric with isethionic acid.[11] He found very essential differences, however, in the behaviour of the two acids towards potassium hydroxide. Whilst the former acid was converted, on simply boiling with this reagent, into alcohol and potassium sulphate, the latter acid was only decomposed on fusion with it and gave rise to the formation of a sulphate and a sulphite. This reaction induced Liebig to assume the existence of dithionic acid in isethionic acid. Berzelius, who adopted Liebig's view, employed it in arranging into two classes the substances produced by the action of sulphuric acid upon organic compounds.[12]

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[7] Ann. Chim. [3] 44, 304; compare also Hunt, *loc. cit.*

[8] Pogg. Ann. 27, 267.

Kolbe, in 1844, tried to bring into harmony with the opinion of Berzelius,[13] the ingenious views of Mitscherlich[14] in accordance with which (following the analogy of the ordinary acids) the sulpho-derivatives of the first class were regarded as compounds of sulphuric acid, and those of the second class as compounds of carbonic acid. He was at that time engaged upon an examination of the substance discovered by Berzelius and Marcet[15] in acting with chlorine upon carbon bisulphide. He fixes its formula as CCl_2SO_2 [$C = 6, O = 8, S = 16$] and calls it sulphite of perchloride of carbon. By treatment with potash he converts this substance into *Chlorkohlenunterschwefelsäure* (trichlormethyl-sulphonic acid), which, in turn, is converted by means of the reaction of Melsens[16] (that is, by the action of nascent hydrogen) into *Chlorformylunterschwefelsäure* (dichlormethyl-sulphonic acid), *Chlorelaylunterschwefelsäure* (chlormethyl-sulphonic acid), and *Methylunterschwefelsäure* (methyl-sulphonic acid). Kolbe regards these compounds as hyposulphuric (dithionic) acid coupled with different radicals, and writes their formulæ :—

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[9] Ann. Chim. [2] **39**, 153; **42**, 222; Pogg. Ann. **15**, 20.

[10] Annalen. **13**, 28.

[11] Compare p. 131.

[12] Annalen. **28**, 1.

[13] Ibid. **54**, 145.

[14] Ibid. **9**, 39; Pogg. Ann. **31**, 283; compare also Mitscherlich, Lehrbuch, Third Edition, **1**, 107 and 586.

[15] Gilb. Ann. **48**, 161.

[16] Compare p. 171.

$C_2Cl_3 + S_2O_5 + HO$	Chlorkohlenunterschwefelsäure.
$C_2HCl_2 + S_2O_5 + HO$	Chlorformylunterschwefelsäure.
$C_2H_2Cl + S_2O_5 + HO$	Chlorelaylunterschwefelsäure.
$C_2H_3 + S_2O_5 + HO$	Methylunterschwefelsäure.

Kolbe succeeds in effecting the synthesis of trichloracetic acid in a similar manner, that is, by treating chloride of carbon with chlorine in sunlight, in presence of water. In this he finds a ground for the assumption by Berzelius of the presence of chloride of carbon in trichloracetic acid, and thereby secures an important footing for Berzelius' whole mode of regarding these compounds. At the same time the analogy of the substance discovered by Dumas, with the compounds containing sulphur, prepared by Kolbe, is now furnished, since trichloracetic acid was written, after the style of Berzelius, $C_2Cl_3 + C_2O_3 + HO$. It was thus a conjugated oxalic acid, whilst the others were conjugated hyposulphuric acids.

Kolbe admits, as Berzelius had done previously, the replacement of hydrogen by chlorine in the copula. That a substitution of this kind should be possible without essential alteration of the properties, depended upon the assumption that the nature of the copula exercised only a subordinate influence upon the character of the compound. Kolbe, no doubt, perceives (what Berzelius never admitted) that he thereby adopts an essential point in the theory of substitution.

It appears to me necessary to state distinctly that Kolbe, and also Frankland (who, at that time, agreed completely with Kolbe's views), adopt the conception of a radical in its earlier sense. They believe in the existence in compounds of certain atomic groups, and are, therefore, far from admitting, with Gerhardt, that different radicals may be assumed to be present in a substance. Both Kolbe and Frankland attack the problem of ascertaining the constitution of compounds, and, by doing so, they essentially distinguish themselves from the adherents of the theory of types who, with the exception of Williamson,[17] write reaction or decomposition formulæ only.

With the assumption of distinct atomic groups in complex substances the idea of the possibility of their isolation was also combined, and thus we find Kolbe and Frankland, in 1848, engaged in experiments which have for their aim the separation of radicals;[18] in particular, it appeared to Kolbe extremely desirable to decompose acetic acid into methyl and oxalic acid, of which it was the conjugated compound. He succeeds in isolating one, at least, of the radicals[19] by aid of the electrical current. Under the influence of this agency, acetic acid splits up into methyl and carbonic acid. According to Kolbe, the reaction took place in such a manner that the conjugated groups first separated from one another, and that the oxalic acid was then converted into carbonic acid at the expense of the oxygen of the water; and the simultaneous evolution of hydrogen appeared to confirm this view.

The preparation of methyl cyanide by heating ammonium acetate with phosphoric anhydride,[20] discovered a short time previously by Dumas, told in favour of the views of Kolbe and Frankland, and so did the conversion of the nitriles into the corresponding acids, which was carried out by the latter chemists themselves.[21]

Upon his isolation of ethyl from ethyl iodide by means of zinc,[22] it appeared to Frankland that he had removed every doubt as to the accuracy of his and Kolbe's mode of regarding compounds. The ethyl theory was now to resume its old place, in the form stated by Liebig in 1835. According to Frankland: "The isolation of four of the compound radicals belonging to the alcohol series, now excludes every doubt of their actual existence, and furnishes a complete and satisfactory proof of the correctness of the theory propounded by Kane, Berzelius, and Liebig fifteen years ago."[23]

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[17] Journ. Chem. Soc. **4**, 350; A. C. R. **16**, 41. [18] Journ. Chem. Soc. **1**, 60; Annalen. **65**, 269. [19] Journ. Chem. Soc. **2**, 157; A. C. R. **15**, 17; Annalen. **69**, 257. [20] Comptes Rendus. **25**, 383 and 473; Annalen. **64**, 332. [21] Annalen. **65**, 288. [22] Journ. Chem. Soc. **2**, 263; Annalen. **71**, 171.

This series of investigations, carried out between 1844 and 1850, rehabilitated the theory of copulæ. Even if it only appeared to be justified by the reactions in the case of a small class of substances, still it was justified for the most important compounds, and for those, in particular, which had influenced Berzelius in setting up his views. Experiment had shown that the assumption of methyl in acetic acid, of chloride of carbon in trichloracetic acid, of ethyl in alcohol, etc., had a real foundation, and it soon appeared to be clear that the way opened up by Kolbe and Frankland must further lead to many brilliant discoveries.

While occupied with the isolation of ethyl from ethyl iodide, Frankland discovered zinc ethyl,[24] a substance which commanded the greatest interest on account not only of its physical but also of its chemical properties. After the discovery of this compound, the efforts of no small number of chemists were directed towards making it available for synthetical purposes;[25] and even although all the hopes which were based upon it were not realised, still there are few compounds which have been employed in so many ways in investigations in organic chemistry. Intimately connected with the discovery of zinc ethyl is the preparation of the other organo-metallic compounds. We are indebted to Wöhler[26] for the discovery of tellurium ethyl; the antimony compounds were prepared by Löwig and Schweizer,[27] and the tin compounds simultaneously by Frankland[28] and by Löwig;[29] mercury ethyl was prepared by Frankland,[30] and aluminium ethyl was prepared by Cahours[31] but first studied by Buckton and Odling.[32] Highly important was the discovery of potassium and of sodium ethyl which was made by Wanklyn,[33] whilst Friedel and Crafts [34] showed how to obtain silicon ethyl, etc.

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[23] Journ. Chem. Soc. **3**, 46; Annalen. **74**, 63.

[24] Journ. Chem. Soc. **2**, 297; Annalen. **71**, 213.

[25] Pebal and Freund, ibid. **118**, 1; Wurtz, Comptes Rendus. **54**, 387; Annalen. **123**, 202; Rieth and Beilstein, ibid. **124**, 242; **126**, 241; Alexeyeff and Beilstein, Comptes Rendus. **58**, 171; Butlerow, Zeitschrift für Chemie. **7**, 385 and 702; Friedel and Ladenburg, Annalen. **142**, 310; Lieben, ibid. **146**, 180, etc.

[26] Ibid. **35**, 111; **84**, 69.

[27] Ibid. **75**, 315.

[28] Phil. Trans. 1852, 418; Annalen. **85**, 332.

[29] Ibid. **84**, 308.

[30] Journ. Chem. Soc. **3**, 324; Annalen. **77**, 224.

[31] Ibid. **114**, 227 and 354

I have intentionally referred to these compounds here because they exercised a distinct influence upon the further development of the theory of conjugated radicals. Kolbe was the first to explain correctly the nature of cacodyl; he calls it methyl coupled with arsenic, $As \frown CH_3$ [C = 6]; [35] and even if we do not now employ the word "coupled," still we have in other respects retained this view with regard to the substance, and our conception of the relation of the metal to the radical has not become much clearer.

Kolbe has a similar way of looking at other organic compounds; all of them contain conjugated radicals, most of them with carbon as the copula. Thus, in acetic acid and the allied compounds, he assumes the radical $C_2 \frown C_2H_3$ which, following the example of Liebig, he calls acetyl; [36] and he writes:—

$(C_2H_3) \frown C_2O$, HO Aldehyde,
$(C_2H_3) \frown C_2O_3$, HO Acetic acid,
$(C_2H_3) \frown C_2Cl_3$ Regnault's chloride of acetyl,[37]
$(C_2H_3) \frown C_2\begin{cases} O_2 \\ NH_2 \end{cases}$ Acetamide [C = 6, O = 8].

Although this formula for acetic acid does not differ essentially from that of Berzelius, still there was much that was new and valuable in the considerations underlying these symbols. For example, Kolbe now draws attention to the fact that the four carbon equivalents of acetic acid (equivalents in Gmelin's sense) do not really possess the same function, but that two of them are contained in it in the form of methyl, while the other two serve as a place for engaging the affinity of the oxygen.

The formulæ of the other fatty acids are obtained from that of acetic acid by replacing the methyl by ethyl, propyl, amyl, etc., while in benzoic acid the radical phenyl occupies the place of the methyl. In general, Kolbe employs the so-called homologous and isologous radicals as equivalent to one another, just as Gerhardt had done.

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[32] Proc. Roy. Soc. **14**, 19; Annalen. Supplementband **4**, 109. [33] Proc. Roy. Soc. **9**, 341; Annalen. **108**, 67. [34] Ibid. **127**, 31. [35] Ibid. **75**, 211, and **76**, 1. [36] Compare p. 137. [37] Annalen. **33**, 319.

The radical ethyl is assumed in alcohol, which Kolbe writes $(C_4H_5)O, HO$, as Liebig also did, only with different atomic weights; on oxidation it splits into C_2H_3 and C_2H_2, and the latter is then converted further into C_2O_2. This explanation is complicated in comparison with the one given by Williamson, but still it afterwards led to important conclusions (see p. 237).

Kolbe formulated Leblanc's monochloracetic acid,[38] and Dumas' trichloracetic acid—

$$HO\left(C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right\}\right)\overset{\frown}{C_2}, O_3 \text{ and } HO(C_2Cl_3)\overset{\frown}{C_2}, O_3.$$

The formulæ become much more complicated in the case of the products obtained by the action of sulphuric acid upon organic acids, where the mode of writing them approximates to that proposed by Dumas and Piria for the "acides conjugés."[39] Sulphacetic acid, for example, becomes

$$2HO\left\{C_2\left\{\begin{matrix}H_2\\SO_2\\SO_3\end{matrix}\right\}\overset{\frown}{C_2}, O_3\right\}$$

Kolbe is still undecided at this time as to whether he should admit the existence of dibasic acids, and he, therefore, retains the old formulæ. Accordingly, oxalic acid is HO, C_2O_3, and succinic acid is $HO, (C_2H_2)C_2O_3$.

It is also worthy of mention that Kolbe assumes radicals containing oxygen in anisic and in salicylic acids, and that he, therefore, no longer agrees with Berzelius upon this point.

In addition to the conjugated metallic radicals and carbon radicals, Kolbe also recognises radicals containing sulphur, and thus the analogy, already noticed, between the ordinary and the sulpho-acids, is preserved. Thus, we have, for example,

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[38] Ann. Chim. [3] 10, 212.

[39] Annalen. 44, 66.

$\mathrm{HO(C_2Cl_3\overset{\frown}{)\,S}_2,\ O_5}$
Chlorkohlenunterschwefelsäure
(Trichlormethyl-sulphonic acid).

$\mathrm{HO(C_2Cl_3\overset{\frown}{)\,C}_2,\ O_3}$.
Chlorkohlenoxalsäure
(Trichloracetic acid).

The paper of Kolbe referred to here forms the complete foundation of a chemical system, from which I have only been able to select the most important parts. In it the attempt is made to maintain the radical theory, but the fundamental conception of this theory has undergone important changes. Thus the capability of radicals to undergo substitution was now necessarily admitted, and, with this admission, the radicals ceased to occupy an exceptional position. Besides this, the conjugated radicals had been tacked on to the theory, and these had not been by any means sharply defined.

Kolbe tries to rescue the electro-chemical theory, but he is obliged to make very important admissions to the opponents of Berzelius. Opposite electrical conditions are still supposed to exist between the constituents of a compound ; but which is the positive and which the negative constituent remains undecided, simply because Kolbe assumes that the same element may possess different electro-chemical properties—an assumption for which justification is found in the existence of elements in allotropic conditions. But the very admission which Kolbe makes, becomes the central point of the controversy; and it is only demonstrated anew that the theory of Berzelius, in the old form, is no longer tenable.

In addition to Frankland, Kolbe had only a few special adherents, and when the former made important changes in the notions with respect to coupling, in 1852, Kolbe, having regard to the facts, was obliged to modify his views. The new hypotheses which he advances, now approach much more nearly to the notion of types, even although his mode of naming and of formulating substances is peculiar to himself. As regards its fundamental principles, the system of Kolbe ranks below that proposed by Gerhardt, particularly because it does not contain any distinction between molecule, atom, and equivalent; but still it also possesses over the latter system, certain advantages which are to be found especially in the greater importance that is attached to the formulæ, and in the breaking up of the radicals containing carbon into simpler ones.

I have just pointed out that, in Kolbe's opinion, the radical (or element) with which a substance is conjugated has only a subordinate influence upon the nature of the compound; Frankland attacks this doctrine in 1852,[40] and he succeeds in convincing Kolbe that it cannot be maintained.

Frankland justifies his views by reference, especially, to the radicals containing metals. In the coupling of arsenic with methyl, the former, according to Frankland, changes its saturating capacity. Whilst it possesses in the free state, the capacity for uniting with five atoms of oxygen, the highest stage of oxidation of cacodyl contains only three atoms of this element. The remaining organo-metallic compounds give occasion to similar considerations, and in consequence Frankland is led to make the following important observations: "When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivs. of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, etc.; and in the five-atom group, NO_5, NH_4O, NH_4I, PO_5, PH_4I, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms. It was probably a glimpse of the operation of this law amongst the more complex organic groups, which led Laurent and Dumas to the enunciation of the theory of types; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts—had they not assumed, that the properties of an organic compound are dependent upon the position and not upon the nature of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done; such an assumption could only have been made at a time when the data upon which it was founded were few and imperfect; and, as the study of the phenomena of substitution progressed, it gradually became untenable, and the fundamental principles of the electro-chemical theory again assumed their sway. The formation and examination of the organo-metallic bodies promise to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable; for, whilst it is evident that certain types of series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electro-chemical character of its single atoms, and not merely upon the relative position of those atoms."[41] It is then pointed out, in conclusion, how "Stibethin furnishes us, therefore, with a remarkable example of the operation of the law of symmetrical combination above alluded to, and shows that the formation of a five-atom group from one containing three atoms, can be effected by the assimilation of two atoms, either of the same, or of opposite electro-chemical character."[42]

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[40] Phil. Trans. 1852, 417; Annalen. **85**, 329.

Frankland, consequently, gives up the idea of coupling, and now regards cacodyl as sulphide of arsenic in which both sulphur atoms are replaced by methyl. He had now adopted, although in a somewhat different form, the theory of types, and if he considers that he really differed from the decided adherents of this theory, inasmuch as he did not assume, with them, "that the properties of an organic compound are dependent upon the position and not upon the nature of its single atoms," I cannot altogether agree with him in this. Since the investigations of Hofmann[43] on substituted bases, the idea of substitution was no longer held, even by Laurent, in the absolute sense in which the latter had at one time stated it.[44] The chlorinated ethers previously prepared by Malaguti[45] could not by any means be brought into harmony with complete invariability of the type; and when Williamson referred ether, alcohol, and acetic acid to the water type, it was plain that he used the word type more in the sense of the mechanical than of the chemical types.

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[41] Phil. Trans. 1852, 441; Annalen. 85, 368. [42] Phil. Trans. 1852, 442; Annalen. 85, 371.

By this paper of Frankland's the first step was taken in the approach towards one another of the heretofore separated schools, and the way to a mutual understanding was provided. It was destined to lead to a fusion of the different opinions, out of which the theory of valency then arose. The change of opinion on the part of Frankland was a gain to the supporters of the theory of types, since he brought with him novel ideas which were capable of being turned to excellent account. I do not assert that they might not themselves have been able independently to make the last great advance—that is, the step to the classification of the atoms according to their valence. In the way in which the development actually took place, the influence of Kolbe, and more particularly that of Frankland, upon the supporters of the Gerhardt-Williamson school (Wurtz, Kekulé, and Odling) can hardly fail to be recognised. Both schools were required, in order to raise the significance of the formulæ to what it subsequently became; especially as Williamson, the only one who desired, even at that time, to write anything more than decomposition formulæ, withdrew from the further development of chemistry.

It may now be expedient to explain at once the transition, for which the way had been prepared by Frankland, from the theory of copulæ to that of types; and then, when I enter upon the consideration of atomicity and of structural formulæ, I shall only need to refer to Kolbe's views, and shall be the better able to point out the influence which he exercised.

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[43] Annalen. **53**, 1.

[44] Comptes rendus par Laurent et Gerhardt, 1845.

[45] Annalen. **24**, 40; **56**, 268.

It was not an easy matter for Kolbe to follow Frankland in his most recent developments; to assume that the affinity of the elements is always satisfied by the same number of atoms without regard to their chemical character, amounted to giving up the electro-chemical theory altogether, and to admitting that the electro-chemical nature of the elements was without influence upon the formation of compounds. Kolbe was not, at first, able to reconcile himself to this.[46] In his Text-book, while recognising the premises of Frankland's arguments, he endeavours to combine these with the electro-chemical principles by means of new hypotheses;[47] and it is only in 1857 that he adopts Frankland's views,[48] which he further develops and turns to account, especially in organic chemistry. He only publishes the detailed statement of the opinions so arrived at, in 1859, in a paper "On the natural relationship of organic to inorganic compounds,"[49] which contains many new ideas.

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[46] Kolbe, Lehrbuch der Chemie 1854, **1**, 20 *et seq.*

[47] As evidence for this statement, which Kolbe attacked as erroneous (J. pr. Chem. [2] **23**, 365), I quote the following passage from Kolbe's Lehrbuch. **1**, 23:—"Frankland felt himself justified in concluding from this that in cacodyl, stibmethyl, stannethyl, etc., a real replacement of different oxygen atoms by the same number of atoms of methyl or ethyl takes place; in other words, that cacodylic acid is arsenic acid which contains two atoms of methyl in place of two atoms of oxygen, and that oxide of stannethyl must be regarded as composed according to the rational formula $\mathrm{Sn}\left\{\begin{matrix}C_4H_5\\O\end{matrix}\right.$, in which the substitution of one atom of oxygen by one atom of ethyl is evident. However little it is possible to agree with this opinion, there can still be no doubt that a regularity does prevail here. The circumstance is perhaps deserving of attention, that, as is well known, those very elements which stand next after potassium in the electro-chemical series—that is, the metals of the alkalies and of the alkaline earths—unite with oxygen in but few proportions; whereas those upon the other side, such as chlorine, sulphur, nitrogen, phosphorus, etc., take up oxygen, on the contrary, in very numerous proportions. Accordingly, when one of these elements by virtue of its coupling with hydrogen or with ether radicals, approaches more closely to potassium in respect to its electro-chemical character and its affinities, its capacity of now uniting with fewer atoms of oxygen than previously, in consequence of this change of position in the electro-chemical series, may probably be found less surprising; although it may not by any means be explained how it comes that the number of atoms of the copula and of oxygen is regularly increased up to a definite number."

Frankland had compared the radicals which contain metals with the corresponding oxides. Kolbe now says that "The chemical organic substances are wholly derivatives of inorganic compounds, and are formed from these, directly to some extent, by extremely simple substitution processes." Carrying out a suggestion made by Liebig,[50] he derives the compounds of carbon from carbonic acid, and those of sulphur from sulphuric acid. The experimental bases of these opinions are the work partly of Mitscherlich,[51] partly of himself (compare p. 224 *et seq.*), and partly also of Wanklyn,[52] who had succeeded in preparing propionic acid from sodium ethyl and carbonic acid.

Kolbe employed at this time, as well as long afterwards, the atomic and equivalent weights of Gmelin, adopting at the same time molecular weights for the majority of compounds agreeable to the determinations of Gerhardt, Laurent, and Williamson. Accordingly he writes carbonic acid C_2O_4, and from this anhydride he apparently derives the organic compounds such as acids, aldehydes, ketones, alcohols, etc. I say "apparently," for I shall afterwards show that it is not really so; but I shall, in the first place, state Kolbe's system in the form in which he applied it.

In carbonic acid, oxygen atoms are distinguished from one another according to whether they are within, or outside of the radical. The formula is therefore written $(C_2O_2)O_2$, carbonic oxide being regarded as the radical of carbonic acid. When an atom of oxygen outside the radical is replaced by hydrogen or an alcohol radical, the series of the fatty acids is obtained:—

$HO, H \quad (C_2O_2)\,O$ Formic acid,

$HO, C_2H_3\,(C_2O_2)\,O$ Acetic acid, etc.

When the second oxygen atom also is replaced by an alcohol radical, a ketone is formed, and when it is replaced by hydrogen an aldehyde is formed :—

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[48] Annalen. **101**, 257. [49] Ibid. **113**, 293. [50] Ibid. **58**, 337. [51] Ibid. **9**, 39. [52] Journ. Chem. Soc. **11**, 103; Annalen. **107**, 125.

$$\left.\begin{matrix}H\\C_2H_3\end{matrix}\right\}C_2O_2 \text{ Aldehyde ; } \left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}C_2O_2 \text{ Acetone.}$$

By the replacement of three atoms of oxygen by three of hydrogen, or by two of hydrogen and a radical, the alcohols are obtained :—

$$HO \quad H_3 \quad C_2, O \quad \text{Methyl alcohol.}$$
$$HO \left.\begin{matrix}H_2\\C_2H_3\end{matrix}\right\}C_2, O \quad \text{Ethyl alcohol, etc.}$$

If this mode of deriving substances is more minutely examined, we recognise that Kolbe's procedure is not altogether justified. By the replacement of an atom of oxygen in carbonic acid by hydrogen, HC_2O_3 is obtained, and not formic acid. Kolbe simply adopts from the dualists the error of sometimes adding HO to the formula and sometimes omitting it. It is true that he states a reason for his doing so, inasmuch as the basicity of a compound (and therefore also the number of HO groups) is determined, according to him, by the number of oxygen atoms outside the radical. Thus nitric acid is monobasic, since it is $(NO_4)\ O$; sulphuric acid is dibasic because it contains two oxygen atoms outside the radical $(S_2O_4)\ O_2$; and phosphoric acid is tribasic $(PO_2)O_3$.

Since, in accordance with this mode of regarding the matter, every atom of oxygen outside the radical carries with it one OH group, when Kolbe speaks of the replacement of such an atom of oxygen, this means that $O + OH = O_2H$ is substituted ; and, taken in this sense, the view can be sustained in a strictly logical manner. It is necessary, however, to start from the hypothetical hydrated carbonic acid $2HO, (C_2O_2)\ O_2$.

By the replacement of

O_2H	by H	we get	$HO,H(C_2O_2)O$	Formic acid,
O_2H	,, C_2H_3	,,	$HO,(C_2H_3)(C_2O_2)O$	Acetic ,,
$2O_2H$	,, H_2	,,	$\left.\begin{matrix}H\\H\end{matrix}\right\}C_2O_2$	Methylaldehyde,
$2O_2H$	,, $(C_2H_3)_2$	,,	$\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}C_2O_2$	Acetone,

O_2H by H and of O_2 by H_2 HO,H_3C_2,O Methyl alcohol,
O_2H „ C_2H_3 „ O_2 „ H_2 HO, $\left.\begin{matrix}H_2\\ C_2H_3\end{matrix}\right\}C_2$,O Ethyl alcohol.

On the conversion of the alcohols into the corresponding acids, the two hydrogen atoms are replaced again by oxygen equivalents. Kolbe's view is now more definite than Williamson's. Whereas the latter assumes the conversion of the radical C_2H_5 into C_2H_3O [C = 12], according to Kolbe, $C_2\begin{matrix}O_2\\ C_2H_3\end{matrix}$ is produced from $C_2\left\{\begin{matrix}H\\ H\\ C_2H_3\end{matrix}\right.$. The difference is important, and it leads Kolbe to foresee the existence of a new class of alcohols, which he announces as follows :—[53]

"If the undernoted formulæ, by means of which I previously represented the rational composition of acetic acid, and of the corresponding aldehyde and alcohol, are inspected—

HO. $(C_2H_3)\,[C_2O_2]$ O	Acetic acid,
$\left.\begin{matrix}C_2H_3\\ H\end{matrix}\right\}[C_2O_2]$	Aldehyde,
HO. $\left\{\begin{matrix}C_2H_3\\ H_2\end{matrix}\right\}C_2$,O	Alcohol,

it will be understood, at the first glance, how it comes that of the five hydrogen atoms in the ethyl oxide of the alcohol, only two are substituted in the oxidation of the latter and only one in that of aldehyde. It is those atoms of hydrogen in alcohol and in aldehyde which stand by themselves that are subject to the oxidising influences, and that present themselves to the oxygen as points of attack far more easily accessible than the other hydrogen atoms which are more firmly held in the methyl radical.

"The above conceptions of the chemical constitution of the alcohols reveal to us the prospect of the discovery of new alcohols as yet unknown, as well as of a new class of substances which, while closely related to the alcohols in respect to their composition, will also probably share many properties with them, but must also behave differently from them in many essential points."

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[53] Annalen. 113, 305-306.

These new substances can also be obtained from carbonic acid or the fatty acids by substitution.

We have :—

$2HO\,(C_2O_2),\,O_2$	Carbonic acid,
$HO\ C_2H_3\ (C_2O_2)\,O$	Acetic ,,
$HO \left.\begin{matrix}H\\(C_2H_3)_2\end{matrix}\right\}C_2,\,O$	Alcohol with one hydrogen atom substituted by methyl (dimethyl-carbinol),
$HO\,(C_2H_3)_3\ C_2,\,O$	Alcohol with two hydrogen atoms substituted by methyl (trimethyl-carbinol).

Kolbe goes so far as to prophesy the chemical character of these hypothetical substances. Thus, according to him, alcohol with one hydrogen atom substituted by methyl must yield acetone on oxidation, by virtue of a reaction which is analogous to the conversion of the normal alcohols into aldehydes :—

$$HO \left.\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}C_2,\,O \text{ gives } \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}C_2O_2 \quad \text{Aldehyde,}$$

$$HO \left.\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}C_2,\,O \text{ gives } \left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}C_2O_2 \quad \text{Acetone.}$$

All these conjectures have been justified in the most brilliant manner, and consequently they have exercised a guiding influence upon the development of the considerations regarding constitution. For this reason, I must return to them in the next lecture.

Kolbe now admits the existence of dibasic acids. These acids are produced, according to him, from two "atoms" of carbonic acid by the replacement of two oxygen atoms outside the radical (and therefore of twice O_2H) by bivalent radicals such as ethylene, phenylene, etc.[54] thus :—

$$\text{Succinic acid} \quad 2HO\,(C_4\,H_4)\left\{\begin{matrix}C_2O_2\\C_2O_2\end{matrix}\right\}O_2$$

$$\text{Phthalic ,,} \quad 2HO\,(C_{12}H_4)\left\{\begin{matrix}C_2O_2\\C_2O_2\end{matrix}\right\}O_2.$$

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[54] The idea of polyatomic alcohol radicals is not due to Kolbe, but to Williamson and Wurtz, as the accompanying development of the subject shows.

Tribasic acids are derived in the same way, from three atoms of carbonic acid, by the replacement of three oxygen atoms by trivalent radicals.

Of the other highly interesting matters discussed in the paper, I mention only the mode of regarding the sulpho-acids in which the analogy with the carbon acids, mentioned already, again makes its appearance. Just as the latter may be derived from carbonic acid, so the former may be derived from sulphuric acid. We have—

$2HO\,(S_2\,O_4)\quad O_2$ Sulphuric acid,
$HO\,(C_2\,H_3)\,(S_2O_4)\,O$ Methylsulphonic acid,
$HO\,(C_{12}H_5)\,(S_2O_4)\,O$ Phenylsulphonic „

The dibasic sulpho-acids are produced from two atoms of sulphuric acid :—

$2HO\,(C_2H_2)\begin{pmatrix}S_2O_4\\S_2O_4\end{pmatrix}O_2$ Disulphometholic acid (methylene disulphonic acid),
$2HO\,(C_{12}H_4)\begin{pmatrix}S_2O_4\\S_2O_4\end{pmatrix}O_2$ Disulphobenzolic acid (phenylene disulphonic acid).

Besides these, Kolbe is acquainted with intermediate acids which are derived from an atom of carbonic acid and an atom of sulphuric acid ; amongst them are sulphacetic and sulphobenzoic acids :—

$2HO\,(C_2H_2)\begin{pmatrix}C_2O_2\\S_2O_4\end{pmatrix}O_2$ Sulphacetic acid,
$2HO\,(C_{12}H_4)\begin{pmatrix}C_2O_2\\S_2O_4\end{pmatrix}O_2$ Sulphobenzoic acid.

This mode of regarding them furnishes a simple explanation of the conversion, observed by Buckton and Hofmann, of sulphacetic acid (really of acetonitrile) into disulphometholic acid by treatment with sulphuric acid.[55] In this operation C_2O_2 is replaced by S_2O_4.

I cannot enter here upon the other points in this extremely important paper, but must advise that a study be made of it, as it is full of clever ideas. It is true that there are views advanced in it with which I cannot agree. Thus, for example, Kolbe did not regard the conception of polyatomicity in the way in which it had been advanced by Williamson, otherwise he could not have inquired why amid-acids with a monobasic radical do not also exist, if these are referred, as was done by Gerhardt and Kekulé, to the type $NH_3 + H_2O$.[56] There can, consequently, be no discussion as to whether Kolbe had not recognised the quadrivalence of carbon before Kekulé. Even although the former rendered unquestionable services with respect to the origination of constitutional or, as Butlerow calls them, structural formulæ, still his participation in the development of the notions as to the atomicity (valency) of the elements and radicals is not of importance, because, as I believe, he did not distinguish between molecule, atom, and equivalent, and also, as follows from the foregoing, because he had not then grasped the idea of the part played by the polyatomic radicals in holding the molecule together.

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[55] Annalen. **100**, 129.

The doctrine of valency was possible, and was bound to ensue as soon as atom and equivalent were separated from each other. If the atoms were not equivalent, the question as to the valency of one when referred to another must necessarily arise. Consequently, those who first distinguished the two ideas from each other, took the first step towards considerations of atomicity, and Dumas, Liebig, and Laurent, must be mentioned in this connection. Whilst the different valency of the elements was recognised by means of the phenomena of substitution, the theory of polybasic acids led to the conception of the polyatomic radicals. Both views remain side by side for a long time without exercising any important influence upon each other, until a fusion of the two took place at the hands of Kekulé ; that is, until the valency of the radicals was explained by that of the elements.

We have already seen in the preceding lecture[57] how Williamson was led to advance the conception of the polyatomic radicals. He employed it to explain the formation of chemical compounds, inasmuch as the polybasic radicals possess the power of holding together several atomic groups. There were but few who then understood the meaning which lay in Williamson's words, and likewise few who recognised the extension that might be given to them. Amongst these, it was Kekulé in particular whose sagacity led him to perceive at once the bearing of Williamson's ideas, and who made use of these ideas to elucidate the relations of thioacetic acid which he had discovered in 1853.[58]

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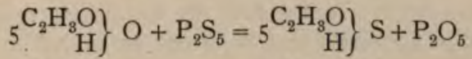
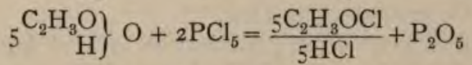
[56] Annalen. 113. 324.

[57] Compare p. 214.

Kekulé compares the reactions of phosphorus pentachloride and of phosphorus pentasulphide upon acetic acid, writing :—



$$5\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + P_2S_5 = 5\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S + P_2O_5$$



$$5\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + 2PCl_5 = \frac{5C_2H_3OCl}{5HCl} + P_2O_5$$

$$[C = 12,\ O = 16,\ S = 32,\ \text{etc.}]$$

Referring to this he remarks :—"The above diagram . . . exhibits . . . the relations between the reactions obtained with the chlorine and with the sulphur compounds of phosphorus. In fact, it is perceived that the decomposition is, in its essential features, the same ; *only*, when the chlorides of phosphorus are employed, the product breaks up into chlorothyl [C_2H_3OCl] and hydrochloric acid, . . . whereas when the sulphur compounds of phosphorus are employed, both groups remain united, because the quantity of sulphur which is equivalent to the two atoms of chlorine is not divisible."

These points of evidence lead Kekulé to declare in favour of the accuracy of the "new atomic weights" (Gerhardt's equivalents). These, according to Kekulé, are a better expression of the facts than the mode of representing them previously in use. Even if the new formulæ are adopted, and the old equivalents retained, it cannot be perceived why phosphorus sulphide produces mercaptan from alcohol whilst phosphorus chloride forms ethyl chloride and hydrochloric acid (C_4H_5Cl and HCl) ; why the latter do not remain combined just as

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[58] Annalen. **90**, 309.

C_4H_5S and HS do, etc. It is not merely a difference in the mode of representing them, but it is a real fact that an atom of water contains two atoms of hydrogen, and only one of oxygen ; also that the quantity of chlorine equivalent to one indivisible atom of oxygen is divisible by two, whereas the sulphur, like oxygen, is dibasic, so that one atom is equivalent to two atoms of chlorine.[59]

The investigations by Frankland, of the radicals containing metals, and his views as to saturating capacity (compare p. 231) had an important influence upon the development of the theory of polyatomic radicals, as also had the interesting paper on salts by Odling, and the important researches of Berthelot on glycerine and of Wurtz on glycols. We shall consider these more minutely.

Odling[60] makes a distinct advance by applying the idea of polybasicity to the metals also, and by reintroducing molecular formulæ for all salts, even for those of the sesquioxides, for which Gerhardt had written equivalent formulæ. He not only refers the polyatomic acids to condensed types, as Williamson had done before him, but he is also acquainted with polyatomic bases, which can be regarded in a similar way. Thus, for example, he writes :—

Oxide of Bismuth $\left.\begin{matrix}Bi'''\\Bi'''\end{matrix}\right\} 3O$; Nitrate of Bismuth $\left.\begin{matrix}3NO_2'\\Bi'''\end{matrix}\right\} 3O$.[61]

Those metals which possess, according to Gerhardt, various equivalent weights, now have several atomicities assigned to them. Odling knows, for example, monatomic and triatomic iron, and monatomic and diatomic tin, whence he obtains the following formulæ :—

Ferric oxide $\left.\begin{matrix}Fe_2'''\\Fe_2'''\end{matrix}\right\} O_3$ corresponding to citric acid $\left.\begin{matrix}C_6H_5O_4'''\\H_3\end{matrix}\right\} O_3$

Ferrous oxide $\left.\begin{matrix}Fe'\\Fe'\end{matrix}\right\} O$,, nitric ,, $\left.\begin{matrix}NO_2\\H\end{matrix}\right\} O$.

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[59] Annalen. **90**, 314. [60] Journ. Chem. Soc. **7**, 1. [61] Odling indicates the atomicity of the elements by means of the dashes to the right of their symbols.

His conception of the acids of phosphorus is likewise interesting. Odling writes:—

Ordinary phosphoric acid	$\left.\begin{matrix}PO'''\\H_3\end{matrix}\right\}O_3$
Pyrophosphoric acid	$\left.\begin{matrix}P_2O_2{}^{\text{vi}}\\H_4\end{matrix}\right\}O_5$
Metaphosphoric acid	$\left.\begin{matrix}PO'''\\H\end{matrix}\right\}O_2$
Phosphorous acid	$\left.\begin{matrix}PO''PH_2'''\\H_4\end{matrix}\right\}O_5$
Hypophosphorous acid	$\begin{matrix}PH_2'''\\H\end{matrix}\ O_2.$

According to Odling, therefore, phosphorous acid stands to pyrophosphoric acid in the same relation as hypophosphorous acid to metaphosphoric acid. A similar relation exists between dithionic and sulphuric acid on the one hand, and oxalic acid and carbonic acid on the other:—

$\left.\begin{matrix}CO\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}S_2O_4\\H_2\end{matrix}\right\}O_2$
Carbonic acid.	Oxalic acid.	Sulphuric acid.	Dithionic acid.

Kay, a pupil of Williamson's,[62] almost simultaneously published a research (obviously suggested by his teacher) which deserves our notice. By the action of sodium ethylate upon chloroform, he had obtained an ether which he called tribasic formic ether, and which had been produced according to the following equation:—

$$\begin{matrix}CH\\Cl_3\end{matrix} + 3\begin{matrix}C_2H_5\\Na\end{matrix}O = \begin{matrix}CH\\(C_2H_5)_3\end{matrix}O_3 + 3\,NaCl.$$

Williamson specially draws attention to the fact that the residues of three molecules of alcohol are held together in the new substance by the trivalent radical CH. This was the first example of a polyatomic hydrocarbon radical, and it was soon to be shown how valuable was this mode of regarding the substance. Berthelot, occupied at the time with the investigation of glycerine (which was completed in

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[62] Proc. Roy. Soc. 7, 135.

1854 so far as its most important parts were concerned),[63] found the very important result that glycerine can unite with acids in three different proportions. Thus:

Monostearine = 1 Glycerine + 1 Stearic acid − 2 Water
$= C_6H_8O_6 + 2\ C_{36}H_{36}O_4 - 2\ HO$
$[C = 6,\ O = 8]$

Distearine = 1 Glycerine + 2 Stearic acid − 4 Water
$= C_6H_8O_6 + 2\ C_{36}H_{36}O_4 - 4\ HO$
(In the paper 2 HO is given.)

Tristearine = 1 Glycerine + 3 Stearic acid − 6 Water
$= C_6H_8O_6 + 3\ C_{36}H_{36}O_4 - 6\ HO$

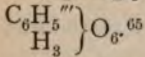
Monochlorhydrine = 1 Glycerine + 1 Hydrochloric acid − 2 Water
$= C_6H_8O_6 + HCl - 2\ HO$

Dichlorhydrine = 1 Glycerine + 2 Hydrochloric acid − 4 Water
$= C_6H_8O_6 + 2\ HCl - 4\ HO$

Berthelot interprets these facts in the following manner:—

"These facts show us that glycerine exhibits the same relation to alcohol that phosphoric acid does to nitric acid. In fact, whilst nitric acid does not produce more than one series of neutral salts, phosphoric acid gives rise to three distinct series of neutral salts, the ordinary phosphates, the pyrophosphates, and the metaphosphates. These three series of salts, when decomposed by powerful acids in presence of water, reproduce one and the same phosphoric acid.

"Likewise, whilst alcohol only produces one series of neutral ethers, glycerine gives rise to three distinct series of neutral compounds. These three series, on complete decomposition in presence of water, reproduce one and the same substance, glycerine."

This comparison between glycerine and phosphoric acid on the one hand, and alcohol and nitric acid on the other, is of great importance, even although it is unfortunately to some extent impaired by taking account of pyrophosphoric and metaphosphoric acids. Odling's orthophosphoric acid[64] has neither the same composition nor the same basicity as these two latter acids, whilst it is always the same substance, glycerine, which is contained in the ethers prepared by Berthelot. Wurtz was happier in his view of these remarkable facts, looking, as he did, upon glycerine as a triatomic alcohol, and representing it as  $\left.\begin{matrix}C_6H_5{}'''\\ H_3\end{matrix}\right\}O_6$.[65] The compounds examined by Berthelot are produced, according to Wurtz, by the replacement of one, two, and three hydrogen atoms by acid radicals. In this connection he points out how the monatomic group C_6H_7 passes into the trivalent residue C_6H_5 by loss of H_2. [$C=6$, $O=8$.]

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[63] Comptes Rendus. **38**, 668; Ann. Chim. [3] **41**, 216; Annalen. **88**, 304; **92**, 301.

It could not escape the notice of a clever investigator like Wurtz that the existence of monatomic and of triatomic alcohols necessarily involves that of diatomic alcohols, and he at once institutes experiments which have for their aim the preparation of such substances. From his way of looking at the subject he necessarily expected a diatomic radical in the still hypothetical alcohol; the univalent group C_6H_7 and the trivalent group C_6H_5 rendered possible the formation of the monatomic and of the triatomic alcohols; the homologues of C_6H_6 must correspond to the diatomic alcohols.[66] The chlorides and bromides which were already well known (in part, at least) favoured the accuracy of this view, and it was now simply a question of converting them into the corresponding hydroxy-compounds and the object was attained. The action of the basic hydroxides did not realise the hopes which Wurtz had entertained, but earlier experiences now came to his aid. Four years previously, he had discovered a reaction whereby a similar conversion could be carried out;[67] and this reaction had subsequently proved serviceable in several cases.[68] It was now to appear that it deserved to be called a general method. Thus, by heating ethylene iodide with silver acetate, Wurtz obtained an acetic ether, which, on decomposition with potash, yielded the desired alcohol:—

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[64] Phil. Mag. [4] **18**, 368.

[65] Ann. Chim. [3] **43**, 492.

[66] Compare Odling, Journ. Roy. Inst. **2**, 62.

[67] Comptes Rendus. **35**, 310; **39**, 335; Ann. Chim. [3] **42**, 129.

[68] Zinin, Annalen. **96**, 361; Cahours and Hofmann, ibid. **100**, 356.

$$C_4H_4I_2 + 2\left.\begin{matrix}C_4H_3O_2\\Ag\end{matrix}\right\}O_2 = \left.\begin{matrix}C_4H_4\\C_4H_3O_2\end{matrix}\right\}O_4 + 2AgI$$

$$\left.\begin{matrix}C_4H_4\\C_4H_3O_2\end{matrix}\right\}O_4 + 2\,KHO_2 \qquad = \quad \left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4 + 2\left.\begin{matrix}C_4H_3O_2\\K\end{matrix}\right\}O_2.$$

In this way Wurtz succeeded in preparing glycol, the first of the diatomic alcohols.[69] He was well rewarded for the difficulties of the investigation, for it is seldom that the discovery of a single substance has exercised such an influence upon the development of chemistry, and seldom that a single compound has given rise to such a series of elegant and useful investigations as this glycol did. I may be permitted to justify this assertion by making some observations with respect to the compounds which stand in the closest relation to glycol.

By the oxidation of glycol, Wurtz obtained glycollic acid and oxalic acid.[70] The former was identical with the substance that Horsford had prepared from glycocoll ten years previously,[71] the nature of which had been announced by Strecker.[72] In exactly the same way lactic acid is produced from propylene glycol.[73] Wurtz proposed $\left.\begin{matrix}C_6H_4O_2\\H_2\end{matrix}\right\}O_4$ as the formula of the former, regarding it, and also glycollic acid, as dibasic acids.[74] The discovery of ethylene oxide and of the polyethylene alcohols was also of great importance. By the treatment of glycol-chlorhydrine $\left.\begin{matrix}H\\C_4H_4\\Cl\end{matrix}\right\}O_2$,[75] (obtained from glycol by the action of hydrochloric acid) with potash solution, Wurtz obtained the ether of the diatomic alcohol, which stands in the same relation to the latter as the anhydride of sulphuric acid does to the acid :—

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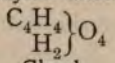
[69] Comptes Rendus. **43**, 199, 1856; compare also **43**, 478; **45**, 306; **46**, 244; **47**, 346. [70] Ibid. **44**, 1306. [71] Annalen. **60**, 1. [72] Ibid. **68**, 55; compare Socoloff and Strecker. **80**, 38. [73] Comptes Rendus. **46**, 1228. [74] Strecker (Annalen. **81**, 247) adopted a formula for lactic acid which was double the above. [75] Comptes Rendus. **48**, 101; **49**, 813; **50**, 1195; **54**, 277.

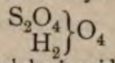
$C_4H_4O_2$
Ethylene oxide.

$S_2O_4.O_2$
Sulphuric anhydride.



$\left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4$

Glycol.

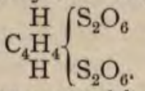


$\left.\begin{matrix}S_2O_4\\H_2\end{matrix}\right\}O_4$

Sulphuric acid.

By heating ethylene oxide with glycol, Wurtz next prepared the polyethylene alcohols[76] which Lourenço had obtained, a short time previously, from ethylene bromide and glycol.[77] The importance of these substances was enhanced by the acids obtained from them by oxidation ;[78] they furnished excellent examples of the formation of substances according to the condensed types such as Wurtz afterwards so well understood how to employ in explaining the silicates.[79] Finally, by the action of ammonia and its analogues, Wurtz obtained from ethylene oxide bases containing oxygen.[80] These substances afterwards became of greater interest in consequence of the synthesis of neurine from glycol-chlorhydrine and trimethylamine.[81]

The adoption of ethylene as a diatomic radical furnished Hofmann[82] with a means of correctly regarding the bases prepared by Cloez in 1853.[83] These now appeared as substances derivable from two molecules of ammonia, and bearing the same relation to glycol that ethylamine does to alcohol. By the further study of these substances,[84] Hofmann succeeded in adducing new proofs of the accuracy of the theory of polyatomic radicals, and in preparing the way to a clear conception of the complicated metal-ammonium compounds.

It would be unjust if I were to close these observations without alluding to H. L. Buff's claim with respect to the recognition of the bivalence of ethylene. Buff, in a preliminary communication, several months prior to the first publication by Wurtz on the subject of glycol, and in a paper laid before the Royal Society one month prior to this publication, had endeavoured to prove the diatomic nature of the hydrocarbons C_nH_n [$C=6$].[85] By treating ethylene chloride with potassium thiocyanate, he had obtained a substance of the formula $C_4H_4Cy_2S_4$, and this, on oxidation with nitric acid, yielded a compound identical with Buckton and Hofmann's disulphetholic acid [86] for which Buff proposes the name ethylene sulphurous acid, representing it by the formula  $C_4\overset{H}{\underset{H}{H_4}}\left\{\begin{matrix}S_2O_6\\ S_2O_6.\end{matrix}\right.$ The formation of ethylene thiocyanate is represented by the equation :—

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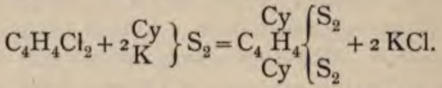
[76] Comptes Rendus. 49, 813. [77] Ibid. 49, 619. [78] Ann. Chim. [3] 69, 317. [79] Répert. de Chimie pure. 2, 449; compare also Leçons de philosophie chimique, Paris, 1864, 181. [80] Comptes Rendus. 49, 898; 53, 338. [81] Ibid. 65, 1015. [82] Ibid. 46, 255. [83] L'Institut. 1853, 213; Jahresbericht. 1853, 468. [84] Proc. Roy. Soc. 10, 224 and 594; Comptes Rendus. 49, 781; 51, 234; Proc. Roy. Soc. 11, 278; Comptes Rendus. 53, 18, etc.



$$C_4H_4Cl_2 + 2\left.\begin{matrix}Cy\\ K\end{matrix}\right\}S_2 = C_4\overset{Cy}{\underset{Cy}{H_4}}\left\{\begin{matrix}S_2\\ S_2\end{matrix}\right. + 2\,KCl.$$

It appears from the whole paper that Buff had recognised the diatomic nature of ethylene, and that, in this respect, he can lay claim to priority over Wurtz. As regards the experimental proof of this view, the two investigations scarcely admit of comparison. The examination of the glycols by Wurtz is amongst the most brilliant achievements of the period; and by its means the hypotheses as to the different valencies of the radicals were provided with so broad a basis that nothing more could be desired in this respect. Buff's experiments conformed to the same theoretical conceptions, but they never could have led to the conclusions which were drawn from the labours of Wurtz.

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[85] Annalen. **96**, 302; Proc. Roy. Soc. **8**, 188.

[86] Annalen. **100**, 129.

LECTURE XIII.

IDEAS REGARDING THE TYPES—ELUCIDATION OF THE NATURE OF THE RADICALS BY THE VALENCY OF THE ELEMENTS—QUADRIVALENCE OF CARBON—SPECIFIC VOLUME—CONSTITUTIONAL FORMULÆ—SEPARATION OF THE IDEAS OF ATOMICITY AND BASICITY—ISOMERISM AMONGST ALCOHOLS AND ACIDS—PHYSICAL ISOMERISM—UNSATURATED SUBSTANCES.

IN the preceding lecture I showed how the views respecting the different valencies of the radicals and elements attained a great importance through the labours of Williamson, Frankland, Kekulé, Odling, Berthelot, Buff, and Wurtz. I shall begin this lecture by showing how the types can be explained by means of these views.[1]

At the period in question Kolbe had attacked Gerhardt's mode of regarding substances as an arbitrary one.[2] Wurtz endeavours to show that this is not so, and that Gerhardt's four types, which, in his opinion, can be reduced to three, represent different states of condensation of matter. Besides the hydrogen type H_2, Wurtz also assumes the types H_2H_2 and H_3H_3. Water, H_2O, formed by the replacement of H_2 by O, corresponds to the former, while ammonia represents triple condensed hydrogen, in which one half of this element is replaced by trivalent nitrogen. Since all of these formulæ correspond to the same volume of the substances in the gaseous state, the view of Wurtz is fully justified. One atom of hydrogen corresponds to one volume, to one half of a volume, or to one third of a volume, according to whether it is present in compounds which belong to the type H_2, H_4, or H_6. Wurtz looks upon the existence of still more highly condensed states of matter as possible, but he does not proceed to introduce types corresponding to these states.

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[1] Ann. Chim. [3] 44, 306. [2] Lehrbuch der Chemie. 1, 50.

It was in 1857, on the occasion of the discussions respecting the constitution of mercury fulminate, that Kekulé [3] first stated that the constitution of this substance, as well as that of the other compounds of the methyl series, may be referred to the marsh gas type, C_2H_4; and to the latter type mercury fulminate is, according to Kekulé's experiments, to be reckoned as belonging.[4]

He therefore writes:—

C_2H_4	Marsh gas.
C_2H_3Cl	Methyl chloride.
C_2HCl_3	Chloroform.
$C_2(NO_4)Cl_3$	Chlorpicrin.
$C_2(NO_4)_2Cl_2$	Marignac's Oil.[5]
$C_2H_3(C_2N)$	Acetonitrile.
$C_2(C_2N)(NO_4)Hg_2$	Mercury fulminate.

A beginning had thus been made, but still the type C_2H_4 was only of very little use. So long as it could not be extended to all carbon compounds, there could be no question of making it the basis of a system of organic chemistry such as it afterwards actually became. The idea which rendered this possible was still wanting. Kekulé had perhaps already conceived it at the time, and merely did not dare to publish it; or it may be that the hypothesis of the linking of carbon atoms had not yet occurred to him. In any case, the views which he then-held must have approximated very closely to those which he published in 1858 concerning the nature of carbon, for, at the end of 1857, when he refers the types to the different valencies of the elements,[6] he definitely mentions the quadrivalence of carbon ; but this is only referred to incidentally, and does not lead him to any further conclusions.

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[3] Annalen. **101**, 200.

[4] [C=6, O=8.] Kekulé here employs these atomic weights again, whereas he had discarded them as inaccurate four years previously. Kolbe (J. pr. Chem. [2] **23**, 374) regards as important the fact that Kekulé then pointed out that he did not employ the word type "in the sense of Gerhardt's unitary theory, but in the sense in which it was first employed by Dumas upon the occasion of his fruitful investigations on the types." I consider this unimportant, more especially as Kekulé proceeds as follows:—"I shall indicate the actual relations in which the substances mentioned stand to one another, by saying that, under the influence of suitable agencies, the one can be produced from, or converted into, the other."

[5] Annalen. **38**, 16.

[6] Ibid. **104**, 129.

At length, in the spring of 1858, the paper appears which has become of such fundamental importance in chemistry.[7] In this paper Kekulé begins to direct attention to the necessity of studying the nature of the elements. This alone, in his opinion, can lead to an explanation of the valency of the radicals. As regards organic chemistry, the chief part in such considerations is played by carbon ; and, consequently, the properties of this element are subjected by Kekulé to a very minute examination. "When the simplest compounds of this element are considered (marsh gas, methyl chloride, chloride of carbon, chloroform, carbonic acid, phosgene gas, sulphide of carbon, hydrocyanic acid, etc.) it is perceived that that quantity of carbon which chemists have recognised as the smallest possible, that is, as an atom, always unites with four atoms of a monatomic or with two atoms of a diatomic element ; that, in general, the sum of the chemical units of the elements united with one atom of carbon is four. This leads us to the opinion that carbon is tetratomic (or tetrabasic)." The hypothesis of the linking of carbon atoms also appears now, and is dealt with in a very detailed manner. "In the cases of substances which contain several atoms of carbon, it must be assumed that at least some of the atoms are in the same way held in the compound by the affinity of carbon, and that the carbon atoms attach themselves to one another, whereby a part of the affinity of the one is naturally engaged with an equal part of the affinity of the other.

"The simplest, and, consequently, the most probable case of such an attachment of two carbon atoms is that in which one unit of affinity of the one atom is united with one of the other. Of the 2 × 4 affinities of the two carbon atoms, two are therefore employed in holding the two atoms themselves together ; six thus remain over which can be held by atoms of other elements."

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[7] Annalen. 106, 129.

On the assumption which is here made, the number of valencies of other elements that can unite with *n* carbon atoms which are united to one another may be expressed by the equation :—

$$n(4-2)+2=2n+2.$$

It is true that this species of mutual union of carbon atoms does not pass with Kekulé as the only one ; he draws attention to the fact that in benzene and its homologues a closer union, "the next simplest," may be assumed.

In order to indicate the standpoint which Kekulé adopted at that time, I may add that, so far as the value of formulæ is concerned, he is a follower of Gerhardt, and does not conceive these as representing the arrangement of the atoms, but merely as reaction formulæ. Accordingly he retains Gerhardt's mode of writing them, and assumes, as the latter had done, that several rational formulæ are possible for one substance. Kekulé is well aware that, starting from the hypothesis of quadrivalent carbon, formulæ may appear in a new guise, but he avoids entering more particularly into the matter. This is comprehensible when we recollect that Kekulé only attaches such a limited significance to formulæ ; since he believes that the physical properties of substances can alone lead to the establishment of hypotheses regarding the arrangement of the atoms. These views possess all the more interest from the fact that it had already been stated in a very influential quarter that two formulæ cannot be assigned to one substance, and that one substance cannot be referred to different types. In collating the results of his excellent investigation on the specific volumes of liquids, Kopp[8] showed that these specific volumes can be calculated from the composition of the substances if a certain specific volume is assigned to each element. This volume is not the same in all cases, however, but is dependent upon the part which the element plays in the compound. Thus, for example, according to Kopp two different specific volumes may be assigned to oxygen, dependent upon whether it exists within or outside the radical. Hence it would not by any means be a matter of indifference, in calculating the specific volumes of aldehydes and of ketones, whether they were referred to the hydrogen or to the water type; whereas Gerhardt had declared both to be admissible.[9] Kopp's rule agreed with the first alternative only. Kopp draws attention to this, and points out that it is exactly in this way that propyl aldehyde is distinguished from the isomeric allyl alcohol :—

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[8] Annalen. 92, 1 ; 95, 121 ; 96, 1, 153, 303 ; 97, 374 ; and especially 100, 19.

$$\left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\} \qquad\qquad \left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}O$$

Propyl aldehyde. Allyl alcohol.

It may certainly be looked upon as a very important sign of the times that the chemists of Gerhardt's school are now forced, upon physical grounds, to attach greater value to their formulæ and speculations than had hitherto appeared to them to be justified. It is true that no special stimulus was now required. Indeed it would appear that Couper had already tried to write real constitutional formulæ. Assuming the quadrivalence of carbon (quite independently of Kekulé) Couper had pointed out how the existence of a great number of organic compounds might be explained. I should like to compare this paper of Couper's[10] with that of Kekulé, published a short time previously, in order to show how these two investigators, starting from different points of view, arrive at very similar results. Kekulé, in recognising and explaining the real essence of the types, hit upon the quadrivalence of carbon and the mutual union of the atoms. Couper, on the other hand, rejects the types because they do not appear to him to satisfy the philosophical requirements which are essential to a theory. According to him, Gerhardt's system rests upon general statements from which individual cases are deduced; whereas he declares the opposite method to be the only correct one. Couper considers it necessary to study first the properties of the elements; and these he regards as:

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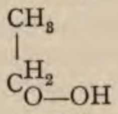
[9] Gerhardt, Traité. 4, 632 and 805. [10] Comptes Rendus. 46, 1157; Ann. Chim. [3] 53. 469.

1. Elective affinity,
2. Degree affinity.

The latter governs the limits of combining capacity, and coincides approximately with what we now call valency or atomicity. In his further consideration of the subject Couper confines himself to the determination of the degree affinity of carbon, and believes that, by means of it, he can elucidate organic compounds. There are two essential properties of this element which serve to characterise it: 1, It combines only with an even number of hydrogen atoms; and 2, It combines with itself. The latter assertion is justified by reference to compounds containing carbon. Hydrogen, oxygen, etc., can be removed from these compounds and their places can be taken by chlorine without interfering with the linking, consequently the cause of this linking cannot be sought for in the atoms capable of substitution. The maximum number of atoms united to one carbon atom is four, and from this Couper obtains for what we should now call saturated organic compounds the expression:—

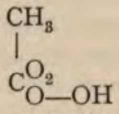
$$nCM_4 - mM_2$$

These observations are sufficient to enable us to understand Couper's formulæ, of which I shall quote a few examples [$C = 12$, $O = 8$]:—[11]



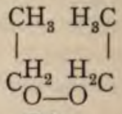
$$\begin{array}{l} CH_3 \\ | \\ C^{H_2}_{O-OH} \end{array}$$

Alcohol.



$$\begin{array}{l} CH_3 \\ | \\ C^{O_2}_{O-OH} \end{array}$$

Acetic acid.



$$\begin{array}{ll} CH_3 & H_3C \\ | & | \\ C^{H_2}_{O-} & {}^{H_2}_{O}C \end{array}$$

Ether.

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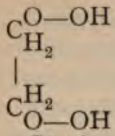
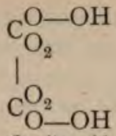
[11] Couper makes curious hypotheses with respect to the properties of the oxygen atom, obviously in order that he may not be obliged to assume in the formation of salts the replacement of the hydrogen by metal (and therefore a reduction of the oxide). According to him $O = 8$ is bivalent, but one valence must always be satisfied by oxygen. The limit of the valency of nitrogen is adopted as 5. (In the paper in Ann. Chim., the formulæ are written on the basis of $C = 6$.)



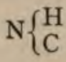
$$\begin{array}{l} C^{O-OH}_{H_2} \\ | \\ C^{H_2}_{O-OH} \end{array}$$

Glycol.



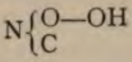
$$\begin{array}{l} C^{O-OH}_{O_2} \\ | \\ C^{O_2}_{O-OH} \end{array}$$

Oxalic acid.



$$N\left\{\begin{array}{l} H \\ C \end{array}\right.$$

Hydrocyanic acid.



$$N\left\{\begin{array}{l} O-OH \\ C \end{array}\right.$$

Cyanic acid.

We here meet, for the first time, with constitutional formulæ in the present sense of the term—with symbols called forth in consequence of the recognition of the atomicity of the elements. In connection with these formulæ it must be remarked that the views as to alcohol and acetic acid represented by them, coincide with those of Kolbe,[12] and that the only differences are in the manner of writing them.

These two papers of Kekulé and of Couper constitute the foundations of our views respecting the structure of compounds. As a consequence of them, organic chemistry took an altogether new direction, and they may be regarded as the most important advances of our science, on the speculative side, in recent times. Adopting the doctrine of the quadrivalence of carbon, the endeavours put forth since that time have been largely directed towards arriving at conceptions regarding the mutual relations of the combining atoms; and I have now to deal with this portion of the historical development of chemistry.

In these considerations respecting constitution, besides the hypothesis as to the nature of carbon, numerous series of experimental data were required; and in view of the fact that the accumulation of the latter was only very incomplete, the labours of years were frequently necessary in order to render possible any application of the principles stated above, to the determination of rational formulæ in the cases of certain classes of substances. Even up to the present we have not succeeded in completely solving this problem, as there are many compounds still which we cannot arrange in the system. What is most important, however, has been accomplished. We are satisfied that the doctrine of atomicity can be employed as the foundation of an edifice, and in this connection, our thanks are due to Kekulé, who, in his excellent text-book, has furnished us with the proofs. Although Kekulé has been reproached from many sides, that in carrying out the principles he had advanced, he does not always adhere to them faithfully —an accusation which is not altogether groundless—still I wish to point out that any such want of adherence only took place in cases where the facts were insufficient at the time for a final decision, and that a quite consistent observance of the principles was, therefore, scarcely possible. It may be pointed out here, however, that at the very time when many difficulties attended the employment of structural formulæ, and when ambiguities frequently arose, Butlerow[13] and Erlenmeyer[14] always advocated with much zeal the consistent maintenance of the principle.

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[12] Compare pp. 235-236.

It is not the business of a historical account to follow in detail the establishment of general principles. Such an account must be confined, rather, to developing the history of the rise and decline of prominent ideas; whereas the enumeration of the facts, and their arrangement from one common view-point, constitute the sum and substance of the science itself, and must, consequently, be dealt with in text-books. I shall therefore content myself by adducing here what was actually of service in strengthening the system, what led to new conceptions or opinions, what appears to be irreconcilable with the principles and leads us to expect an expansion or alteration of the present theories.

I shall begin with a description of the discussion regarding the constitution of lactic acid, which took place within the period 1858-60, and led to the distinction between atomicity and basicity in the case of acids. Following the lead of Gerhardt, who regarded lactic acid as a dibasic acid,[15] many chemists doubled the formula for this acid and wrote it $C_{12}H_{12}O_{12}$ [$C = 6$, $O = 8$], whereas the interesting synthesis of alanine, and the conversion of this compound into lactic acid by Strecker,[16] made the halved formula more probable. Wurtz, in the oxidation of propylene glycol, brought forward a decisive reason for the latter view.[17] At the same time the dibasic character of the acid also seemed to be confirmed, so that Wurtz wrote :—

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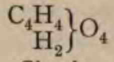
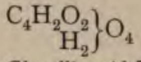
[13] Zeitschrift für Chemie. 4, 549; 6, 500. [14] Ibid. 7, 1. [15] Gerhardt, Traité. 1, 689.



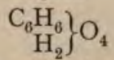
$$\left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4$$

Glycol.



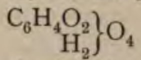
$$\left.\begin{matrix}C_4H_2O_2\\H_2\end{matrix}\right\}O_4$$

Glycollic acid [C=6, O=8].



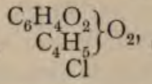
$$\left.\begin{matrix}C_6H_6\\H_2\end{matrix}\right\}O_4$$

Propylene glycol.



$$\left.\begin{matrix}C_6H_4O_2\\H_2\end{matrix}\right\}O_4$$

Lactic acid.

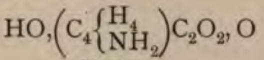


The reaction with phosphorus pentachloride, which yielded the chloride $C_6H_4O_2Cl_2$ (a substance that was converted by alcohol into chlorlactic ether, $\left.\begin{matrix}C_6H_4O_2\\C_4H_5\end{matrix}\right\}O_2, \atop Cl$ corresponding to glycol-chlorhydrine), was a new argument in favour of this view, whilst the vapour density of the chlorlactic ether justified the molecular weight adopted.[18]

Kolbe regards lactic acid as monobasic, and calls it oxypropionic acid, assuming the same relation between it and propionic acid as that between oxybenzoic acid and benzoic acid.[19] In the same way that Gerland was able to convert amido-benzoic acid into oxybenzoic acid (by means of nitrous acid[20]), lactic acid can also be obtained from alanine. The latter and glycocoll were to be regarded as amido-acids—a view which found new support upon the conversion of bromacetic acid into glycocoll by Perkin and Duppa[21]—so that Kolbe was able to write :—

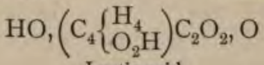
$$HO,(C_4H_5)C_2O_2,O$$

Propionic acid.



$$HO,\left(C_4\left\{\begin{matrix}H_4\\NH_2\end{matrix}\right.\right)C_2O_2,O$$

Alanine.



$$HO,\left(C_4\left\{\begin{matrix}H_4\\O_2H\end{matrix}\right.\right)C_2O_2,O$$

Lactic acid.

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[16] Annalen. **75**, 27. [17] Comptes Rendus. **45**, 306. [18] Ibid. **46**, 1228. [19] Annalen. **109**, 257. [20] Ibid. **91**, 185. [21] Ibid. **108**, 106.

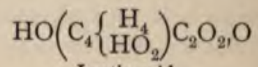
Kolbe tries to bring the substances prepared by Wurtz into harmony with his views, contending that lactyl chloride is chlorpropionyl chloride, which passes, by the action of alcohol, into chlorpropionic ether; as indeed Ulrich obtains propionic ether from it by means of nascent hydrogen.[22] Kolbe could also have adduced, in favour of his ideas, the preparation of glycollic acid from monochloracetic acid which Kekulé had succeeded in effecting,[23] whereas Kekulé discovers in it the conversion of a monobasic into a dibasic acid.[24]

Wurtz now brings forward new proofs in support of the accuracy of his view,[25] finding these in the existence of the dibasic lactates which had been described by Engelhard and Madrell[26] and by Brüning.[27] Further, he succeeds in preparing dibasic lactic ether (by treating chlorpropionic ether with sodium ethylate), and also lactamethan and butyrolactic ether. The reduction of lactic acid to propionic acid by means of hydriodic acid—a reaction discovered by Lautemann[28]—and the conversion of chlorpropionic ether into alanine[29] furnished Kolbe, on the other hand, with new grounds for the assumption that lactic acid is a monobasic oxy-acid. Acids of this kind he defines as monobasic acids in which a hydrogen atom within the radical is replaced by HO_2, hydrogen peroxide.[30] The analogy between the carbonic and the sulphonic acids, already alluded to several times, is employed in support of the views he is now defending, lactic acid being compared with isethionic acid.

Thus:—

$$HO(C_4H_5)C_2O_2,O$$

Propionic acid.

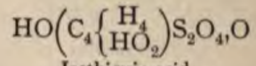


$$HO\left(C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)C_2O_2,O$$

Lactic acid.

$$HO(C_4H_5)S_2O_4,O$$

Ethylsulphonic acid.



$$HO\left(C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)S_2O_4,O$$

Isethionic acid.

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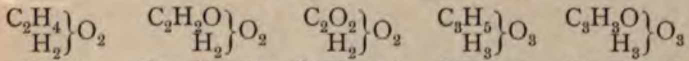
[22] Annalen. **109**, 268. [23] Ibid. **105**, 286; compare also R. Hoffmann, ibid. **102**, 1. [24] Compare also Heidelberger Jahrbücher 1858, 339. [25] Comptes Rendus. **48**, 1092. [26] Annalen. **63**, 93. [27] Ibid. **104**, 191. [28] Ibid. **113**, 217. [29] Kolbe, ibid. **113**, 220. [30] Ibid. **112**, 241.

In this discussion, so far as we have considered it as yet (up to 1859), Kolbe's way of regarding the matter was better adapted to explain the facts than that of Wurtz. In particular, it was possible to explain, in a very satisfactory manner, the relations between the fatty acids and the lactic acids, as well as the phenomena of isomerism amongst the ethers of the latter acids, which Wurtz discovered in the following year.[31] What Kolbe misunderstands, are the relations, pointed out by Wurtz, between the glycols and these acids;[32] and even in 1860, when he returns to the constitution of lactic acid, he still adopts the same standpoint.[33] He emphasises the difference between the two hydrogen atoms, replaceable by radicals, in lactic and glycollic acids; but he does not admit that the hydrogen peroxide groups, which they contain, also occur in the glycols.

Wurtz, meanwhile, has gone a step further. He introduces a distinction between atomicity and basicity in the case of acids.[34] Whilst the former of these is determined by the valency of the radical present, the latter is regulated by the number of hydrogen atoms replaceable by metals. According to Wurtz, "the capacity of saturation of an acid towards basic oxides depends not only upon the number of equivalents of typical hydrogen which it contains, but also upon the electro-negative nature of the oxygenated radical. In proportion as the oxygen increases in this radical, the typical hydrogen becomes more and more basic hydrogen."

This is illustrated by the following example:—



$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2H_2O\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}C_3H_3O\\H_3\end{matrix}\right\}O_3$
Glycol.	Glycollic acid.	Oxalic acid.	Glycerine.	Glyceric acid.
2 typical H atoms.	2 typical H atoms.	2 typical H atoms.	3 typical H atoms.	3 typical H atoms.
	1 basic.	Both basic.		1 basic.

Glyceric acid is triatomic but only monobasic; phosphorous and cyanuric acids are triatomic and dibasic. Further, Wurtz regards lactic acid as dibasic, and as different in constitution from glycollic acid. He is forced to this by the existence of the lactates described by Brüning and others.

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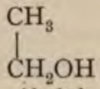
[31] Ann. Chim. [3] **59**, 161. [32] Compare especially Annalen. **109**, 262, etc. [33] Ibid. **113**, 306. [34] Bull. Soc. Chim. **1**, 33; Ann. Chim. [3] **56**, 342.

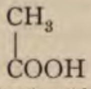
The first part of Kekulé's text-book appeared in the same year, and it was possible to see from it how easily the nature of the lactic acids might be explained by reverting, as Kekulé did, to the elements themselves. For although he too employs the mode of representation according to types, still this is elucidated by means of the so-called graphic formulæ which are intended to express the relationships of the atoms. These formulæ constituted a new mode by which to represent the constitution of compounds. They remained in use for some time, but they were again replaced, at a later date, by written formulæ which approach to those introduced by Couper.

The following are examples of these formulæ :—



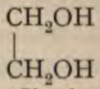
$$\begin{array}{l}CH_3\\|\\CH_2OH\end{array}$$

Alcohol.



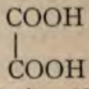
$$\begin{array}{l}CH_3\\|\\COOH\end{array}$$

Acetic acid.



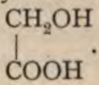
$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}$$

Glycol.



$$\begin{array}{l}COOH\\|\\COOH\end{array}$$

Oxalic acid.

The relations of the atoms in glycollic acid were furnished to Kekulé by the method for its formation from chloracetic acid, which was discovered by himself. These relations can be represented by the formula  $\begin{array}{l}CH_2OH\\|\\COOH\end{array}$. Both glycollic acid and lactic acid contain two typical hydrogen atoms ; that is, as Kekulé now explains,[35] two atoms of hydrogen united to the carbon by means of the oxygen. These two atoms differ in their properties, inasmuch as the one behaves like the typical hydrogen of acetic acid, being influenced by two oxygen atoms, whilst the other plays a part resembling that of the typical hydrogen in alcohol. The solution of the difficulty was now supplied, since this view explained to the adherents of the doctrine of atomicity all the chemical reactions of glycollic acid, as well as its relation to glycol and also to acetic acid. A few years later, Kekulé proved, by the action of hydrobromic acid on these acids,[36] that they are converted by this reagent into the corresponding bromides just as readily as the alcohols are; and thus the views which he had previously stated regarding the existence of "alcoholic hydrogen" in these compounds received new support. Perkin[37] had already tried to confirm the alcoholic nature of glycollic and lactic acids, from the fact that sodium acts upon lactic ether with the evolution of hydrogen, and from the formation of ethereal compounds and the evolution of hydrochloric acid when the acids are treated with acetyl chloride or succinyl chloride. These investigations of glycollic and of lactic acids are also highly important, because it was in connection with them that proof was furnished of the specially noteworthy circumstance that a two-fold function may be ascribed to one and the same substance, the two sets of properties in such a case being simply superadded.

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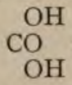
[35] Kekulé, Lehrbuch der Chemie. I, 130 and 174.

Kekulé was also able to explain the fact that carbonic acid, which is homologous with glycollic acid, is a dibasic acid and forms salts with two atoms of metal. The formula of the hypothetical hydrate became  $\mathrm{CO}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}$; both hydrogen atoms were equally influenced by the oxygen, and there was no reason for any difference between them.[38]

It must be specially pointed out here that Kolbe's formula for glycollic acid possesses a great similarity to the one that has just been given, when the signification is alone taken into account and not the form; it was due, no doubt, to his somewhat more complicated mode of writing the formula that Kolbe did not deduce from it all the consequences which it involved. On the whole, the advantages of Kolbe's way of regarding compounds were now about to become more manifest. In 1862, by the addition of hydrogen to acetone,

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[36] Annalen. **130**, 11. [37] Zeitschrift für Chemie. **4**, 161. [38] Kekulé, Lehrbuch. **1**, 739.

Friedel obtained a propyl alcohol[39] identical with that prepared by Berthelot from propylene.[40] Kolbe[41] at once recognised this as the first representative of the group of isomeric alcohols whose existence he had foreseen.[42] He assigned to it the formula $\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}C_2O,HO$, and maintained that the dissimilarity between it and Chancel's fermentation propyl alcohol[43] would be decided by an experiment involving its oxidation, since the new alcohol should thereby yield acetone. Friedel actually proved that it did so.[44]

Kolbe returns to this alcohol two years later.[45] By a comparison of the ammonia bases with the alcohols, he arrives at the conclusion that cases of isomerism must occur amongst the latter, quite similar to those amongst the former :—

$\left.\begin{matrix}C_2H_3\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C_2H_3\\H\\H\end{matrix}\right\}C_2,O,HO$	$\left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}C_2,O,HO$
Methylamine.	Methyl carbinol.	Ethylamine.	Ethyl carbinol.
$\left.\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}C_2,O,HO$	$\left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N$	$\left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}C_2,O,HO$
Dimethylamine.	Dimethyl carbinol.	Trimethylamine.	Trimethyl carbinol.

Kolbe now extends his observations to the acids, and thinks that he can foresee the occurrence of isomerism in this class of substances also. Frankland, at a somewhat earlier date, prepared leucic acid by treating oxalic ether with zinc ethyl,[46] and this interesting synthesis suggested the new ideas to Kolbe. He regards Frankland's acid (as Frankland himself had done) as diethyl-oxyacetic acid, and represents it by the formula $C_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\,O_2\end{matrix}\right\}C_2O_2,O,HO$. It corresponds to diethyl-acetic acid.

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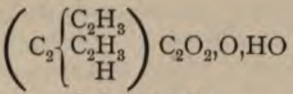
[39] Comptes Rendus. **55**, 53 ; Annalen. **124**, 324. [40] Comptes Rendus. **44**, 1350. [41] Zeitschrift für Chemie. **5**, 687. [42] Compare p. 237. [43] Annalen. **87**, 127. [44] Repert. de Chimie pure. **5**, 247. [45] Zeitschrift für Chemie. **7**, 30 ; Annalen. **132**, 102. [46] Proc. Roy. Soc. **12**, 396 ; Annalen. **126**, 109.

Kolbe is also acquainted with a dimethyl-acetic acid, which he calls isobutyric acid, since it is different, according to him, from ordinary butyric acid:—

$$C_6H_7(C_2O_2)O,HO$$

Butyric acid.



$$\left(C_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right.\right)C_2O_2,O,HO$$

Isobutyric acid.

Kolbe assumes three isomeric substances having the formula of valerianic acid: trimethyl-acetic acid, methyl-ethyl-acetic acid, and propyl-acetic acid. Isomeric derivatives correspond to these compounds, such, for example, as oxy-acids, amongst which Kolbe classes Städeler's acetonic acid.[47]

These views were completely confirmed, and Kolbe's clever prediction thereby achieved a great triumph. Friedel's acetone alcohol was the first compound representative of this class of substances that was prepared, and it, therefore, is of great importance. As the constitution of acetone had been settled by Freund's synthesis, there could scarcely be any doubt as to the formula of the new propyl alcohol; and this formula was employed by Erlenmeyer[48] (after he had found that the alcohol was identical with the one prepared from glycerine[49]) in explaining the constitution of the triatomic alcohol.

The discovery of the "hydrates" by Wurtz[50] followed immediately after the discovery of isopropyl alcohol. Wurtz obtained these substances by treating the hydrocarbons of the ethylene series with hydriodic acid and silver oxide; and he studied their properties particularly in the case of amylene hydrate, where he was able to recognise its difference from amyl alcohol. At first he looked upon this substance as a compound of the hydrocarbon with water, and represented it by the formula C_5H_{10}, H_2O, a view which appeared to be warranted by its ready decomposition into these substances. At a later period he believed that the divergences from the normal alcohols could be explained on the assumption that the union of the hydrogen atom in the hydrates is different from (*i.e.*, less intimate than) that in the substances isomeric with them.[51]

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[47] Annalen. 111, 320. [48] Ibid. 139, 111. [49] Zeitschrift für Chemie. 7, 642. [50] Comptes Rendus. 55, 370; 56, 715, 793; 57, 479.

Kolbe looked on these substances as likewise belonging to the group of secondary alcohols, whose existence he had foreseen,[52] and he tries to prove this by means of an oxidation experiment, which, however, does not furnish any decisive result. Wurtz,[53] who also carries out this experiment, obtains acetone as well as acetic acid. The question thus remained undecided[54] until, at a much later date (in 1878), Wischnegradzky was able to prove that amylene hydrate belongs to the group of tertiary alcohols.[55] These had, however, been discovered much earlier (in 1863) by Butlerow[56] as the products of a very remarkable, complex reaction; but a large number of investigations by Butlerow and his pupils were required in order to establish conclusively the nature of these substances, and their relations to the other alcohols.

With respect to isomerism in the fatty series, Erlenmeyer had obtained isobutyric ether in 1864, by the method proposed by Kolbe,[57] but had not been able to discover any decided difference between it and ordinary butyric ether. Morkownikoff, however, established the difference later by a careful study of the salts;[58] and proved, besides, that acetonic acid is identical with oxy-isobutryic acid.[59] The neat syntheses by Frankland and Duppa are of considerable importance in connection with this question. These chemists succeeded in passing from oxalic acid to substances of the lactic acid series, and then they further converted these into the corresponding members of the acrylic acid series.[60] Further, by means of aceto-acetic ether, which had been discovered by Geuther,[61] they were able to introduce alcohol radicals into acetic acid, and thus to obtain homologues of the latter.[62] Wislicenus afterwards followed up these reactions, and elucidated them more fully. Numerous syntheses were carried out by Wislicenus and his pupils according to this method, and thus our knowledge of the constitution of acids containing a number of carbon atoms was very considerably advanced.

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[51] Zeitschrift für Chemie. **7**, 419.

[52] Annalen. **132**, 102.

[53] Comptes Rendus. **58**, 971.

[54] Ibid. **66**, 1179.

[55] Annalen. **190**, 328.

[56] Répert. de Chimie pure. **5**, 582; Bull. Soc. Chim. [2] **2**, 106; Annalen. **144**. 1.

[57] Zeitschrift für Chemie. **7**, 642.

[58] Annalen. **138**, 361.

[59] Zeitschrift für Chemie. **10**, 434.

[60] Journ. Chem. Soc. **18**, 133; **22**, 28; Phil. Trans. 1866, 309; Annalen. **133**, 80; **135**, 25; **136**, 1; **142**, 1.

[61] Jahresbericht 1863, 323.

The fact established by Schorlemmer,[63] that dimethyl is identical with ethyl hydride, had a distinct value in all considerations with respect to constitution; and so also had the recognition of the identity of carbonic ethers containing two different alcohol radicals [64] (a point that was doubted at first [65]). It was only after these matters had been settled that the similarity of the four valencies of carbon—the first thing necessary in order to inspire confidence in the "structural formulæ" now so commonly employed—could be assumed.

It will be apparent from the researches already mentioned that it is really a part of the business of scientific chemistry to explain the phenomena of isomerism. Cases of isomerism occur so frequently that even the clearest head would not be in a position to survey the facts, if these were simply enumerated without any theoretical assumptions. Experience has shown, however, that graphic or structural formulæ are extremely valuable in explaining known cases of isomerism and in helping us to foresee new ones; and it can thus be understood why the efforts of chemists were more and more directed towards establishing such formulæ. It is obvious that I cannot here take notice of all these efforts, but I must give an exposition of the principle that is adopted in drawing conclusions from the reactions of substances with respect to their constitutions. This principle states that the mutual relations of the atoms remain unchanged during transformations, with the exception of those which are severed, and that with respect to the latter the atoms or groups that enter into the new combinations re-establish similar relations. I do not think I am mistaken in regarding this fundamental principle as a new form of Laurent's law of substitution.[66] It is a generalising of this law, but the law has acquired, at the same time, another meaning, in so far that chemists now no longer desire to determine the arrangement of the atoms in space but only their relations to one another. Unfortunately, no general proof of the principle has been furnished, and experiments have not even been carried out which aim at this. Its accuracy, which is certainly not beyond doubt, is merely assumed because the conclusions drawn from it have repeatedly yielded concordant results; that is, because these conclusions led to identical formulæ for the same substance whichever mode of formation was considered.

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[62] Annalen. **135**, 217; **138**, 204 and 328. [63] Ibid. **131**, 76; compare also Carius, ibid. **131**, 173; and Schöyen, ibid. **130**, 233. [64] Röse, Annalen. **205**, 227. [65] J. pr. Chem. [2] **22**, 353.

Nevertheless, this concordance is not always met with. There are many cases known where the constitution deduced from one mode of formation does not correspond to the formula which may be derived by starting from another mode of formation, or from the decomposition products.[67] In such cases we are obliged to assume the conversion of the substance into an isomeric modification, in one of the reactions that have taken place; that is, we must hold that the principle stated above does not here apply, and that the atoms remaining in the molecule have changed their mutual relations during one of the reactions. Cases of this kind deserve attention. They are well calculated to shake our faith in the accuracy of the fundamental principle, even although an attempt has been made to regard them as two-fold reactions, and in agreement with this principle. A special interest attaches to those investigations that define the conditions under which such isomeric changes—the so-called migration or wandering of the atoms—take place within the molecule, and to those actually designed to elucidate this particular matter. As examples of these, Hofmann's investigation of the conversion of the methyl anilines into homologues of aniline[68] and Demole's examination of the spontaneous oxidation of ethylene derivatives,[69] may be mentioned here.

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[66] Compare pp. 143-144.

[67] Compare, for example, Carius, Annalen, **131**, 172; Tollens, ibid. **137**, 311; Friedel and Ladenburg, ibid. **145**, 190; Linnemann and Siersch, ibid. **144**, 137; Butlerow and Ossokin, ibid. **145**, 257; Simpson, ibid. **145**, 373; Erlenmeyer, ibid. **145**, 365, etc.

Those phenomena of isomerism, however, which cannot be expressed or represented by means of the ordinary formulæ, are of still greater importance. Examples of this nature have long been known, and some of them were minutely studied at an early period. More recently (after the recognition of the importance of the matter) an attempt has been made to introduce a special method of explaining them, which is, no doubt, connected with the theory of valency, but is also a further development and an extension of that theory. We must here enter upon a more particular account of this matter.

The discovery of racemic acid, isomeric with tartaric acid, has already been mentioned in Lecture VII. (p. 118). The recognition of the relations between these two acids forms the subject of an investigation by Pasteur which is of fundamental importance for the subject now to be considered.[70] Pasteur showed that there are four isomeric tartaric acids, viz.: racemic acid, inactive tartaric acid, and right and left rotating tartaric acids. He showed, moreover, that the two latter acids crystallise in similar, but in oppositely built-up (enantiomorph) forms; that they both rotate a ray of polarised light through equal angles, but in opposite senses; and that when mixed in equal quantities they yield optically inactive racemic acid. Further, he succeeded in decomposing racemic acid again into the two optically active tartaric acids, by three different methods:—

1. By preparing and crystallising the sodium-ammonium salt; when two enantiomorph varieties were obtained. These, after having been separated and decomposed, yielded the two tartaric acids.

2. By preparing the cinchonicine and quinicine salts. In

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[68] Berichte. **4**, 742; **5**, 704, etc. [69] Ibid. **11**, 315, 1302, and 1307.

[70] Ann. Chim. [3] **24**, 442; **28**, 56; **38**, 437; compare also Pasteur, Recherches sur la dissymétrie moléculaire des produits organiques naturels. Leçons de chimie, Paris 1861; Alembic Club Reprints, No. 14.

the case of the former the salt of left tartaric acid crystallised first; in that of the latter, the salt of right tartaric acid crystallised first.

3. By treating a solution of acid ammonium racemate with spores of *Penicillium Glaucum*, by which means the salt of left tartaric acid alone remains in the solution after the development of the fungus.

Pasteur prepared inactive tartaric acid by heating cinchonine tartrate; and Dessaignes was able to show that this acid was partially reconverted into racemic acid by heating it to 200°.[71]

Facts of a similar kind have been observed in the cases of various other substances, such, for example, as the glucoses, the terpenes, amyl alcohol, aspartic acid, etc. Exactly the same relations that are observed in the case of tartaric acid occur also in that of mandelic acid, according to experiments by Lewkowitsch.[72]

In all these cases of isomerism it is in their physical properties that the corresponding substances differ from each other; and on this account Carius[73] introduced for such cases the designation physical isomerism.

In 1874 Le Bel[74] and, shortly after him, van 't Hoff[75] endeavoured to explain these facts also upon the theory of atomicity, having first adopted the view that a substance only possesses optical activity when its molecule contains an asymmetric carbon atom; that is, when a carbon atom is present in it which has its four valencies satisfied by union with four atoms or groups all different from one another. This view is warranted by the facts, in so far that all optically active substances known up to the present contain at least one asymmetric carbon atom. It must be stated, however, that by no means all substances which contain asymmetric carbon atoms possess rotating power, and that the view stated above cannot, therefore, be turned about and generalised as if this were so. Van 't Hoff has endeavoured to render the matter clear by means of a geometrical conception as to the arrangement of the atoms in space. This cannot, however, be more fully entered into here.

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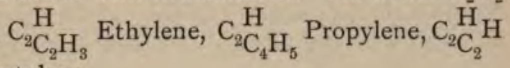
[71] Annalen. **136**, 212. [72] Berichte. **16**, 1565 and 2721. [73] Annalen. **126**, 214; **133**, 130. [74] Bull. Soc. Chim. [2] **22**, 337. [75] Ibid. [2] **23**, 295; compare also La chimie dans l'espace, Rotterdam, 1875; Chemistry in Space, translated and edited by Marsh, Oxford, 1891.

A considerable time ago, Rochleder[76] pointed out that substances belonging to one particular class, very easily undergo isomeric changes; and he called these substances defective because they are produced by the separation of certain atoms from saturated substances. They are now commonly called unsaturated compounds, and we shall consider them particularly, as their study is a subject of great interest.

In his paper on the theory of organic compounds, Couper[77] ascribed to carbon the capacity of bringing sometimes two, and sometimes all four of its units of affinity into play; hence it was not difficult for him to explain the existence of such compounds as carbonic oxide, ethylene, etc. Amongst others, Wurtz[78] and Kolbe[79] fell in with this view. The latter derives the unsaturated hydrocarbons from the type of carbonic oxide, assuming in all of these substances one or several carbon atoms which are active with two affinities. He writes C_2O_2 Carbonic oxide, $C_2\genfrac{}{}{0pt}{}{H}{C_2H_3}$ Ethylene, $C_2\genfrac{}{}{0pt}{}{H}{C_4H_5}$ Propylene, $C_2\genfrac{}{}{0pt}{}{H}{C_2}H$ or $C_2 . C_2H_2$ Acetylene.



Kekulé at first tried to explain the unsaturated substances by the assumption of a denser arrangement of the carbon atoms,[80] but afterwards, in his admirable and important investigations of organic acids[81] he appears to have been of opinion that, in these substances, the affinities of the carbon are not fully satisfied, and that they contain free affinities or blanks. This assumption became more probable both from Kekulé's own experiments and from those of Carius,[82] in accordance with which the substances can combine with hydrogen, chlorine, hypochlorous acid, etc. The capacity for entering into direct additions thus became a characteristic of the group; but it cannot be said to be really distinctive, since some substances which are classed as saturated also possess this capacity. As examples of the latter substances the aldehydes and ketones in particular may be instanced, and these are substances which contain oxygen wholly united to carbon. In explanation of the facts, the assumption is made regarding these compounds that, by addition, the group $(C=O)''$ passes into $(C—O)''''$; that is to say, a diatomic radical becomes a tetratomic one. Later experiments of a very detailed character on the unsaturated acids, by Fittig, have led to the confirmation of the view mentioned above;[83] that is, they have shown that the facts are best accounted for when blanks, or bivalent carbon atoms, are assumed in some compounds at least. That it is not possible to avoid some assumption of this kind is shown by carbonic oxide and by the group of isonitriles or carbylamines, discovered almost simultaneously by Hofmann[84] and by Gautier.[85] The latter interesting substances are obtained by treatment of the amines with chloroform and by the action of the alkyl iodides on silver cyanide. They are isomeric with the nitriles, and their constitution cannot be represented otherwise than by the formula $N\left\{\begin{matrix}R\\C\end{matrix}\right.$, first proposed by Gautier,[86] in which R stands for a monatomic alcohol radical. If the nitrogen is assumed to be trivalent,[87] the carbon then appears as bivalent or unsaturated.

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[76] Ber. Wien. Akad. **11**, 852; **12**, 727; also ibid. **49** (second part), 115.
[77] Ann. Chim. [3] **53**, 469; compare p. 254.
[78] Leçons de philosophie chimique. 136.
[79] Kolbe, Lehrbuch der organischen Chemie. **1**, 738; **2**, 576.
[80] Kekulé, Lehrbuch der organischen Chemie. **1**, 166.
[81] Annalen. **117**, 120; Supplementband **1**, 129, 338; Supplementband **2**, 85; **130**, 1.
[82] Ibid. **124**, 265; **126**, 195; **129**, 167.

There is, besides, a class of unsaturated substances, in which, following Kekulé's lead, a more intimate union of the carbon atoms is quite generally assumed. I refer to the aromatic compounds. Under this heading a number of substances which stand in a close chemical relationship to certain strongly smelling oils were formerly grouped together.

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[83] Annalen. **188**, 95. [84] Ibid. **144**, 114; **146**, 107. [85] Comptes Rendus. **65**, 468; Annalen. **146**, 119. [86] Comptes Rendus. **65**, 901. [87] Quinquivalent nitrogen is referred to in Lecture 15.

Kekulé showed that all these substances may be regarded as derivatives of benzene, and that their chemical nature is dominated by the constitution of this hydrocarbon.[88] A large number of earlier observations told in favour of this view, but some synthetical investigations which had been carried out a short time previously by Fittig in conjunction with Tollens [89] and others [90] were also of importance. These chemists employed a method which originated with Wurtz;[91] that is, they treated mixtures of the alkyl iodides and the bromine substitution products of aromatic hydrocarbons with sodium, whereby they succeeded in preparing homologues of the hydrocarbons in question. They were thus able to show that methyl-benzene, obtained from bromo-benzene and methyl iodide, is identical with toluene, but that ethyl-benzene is different from xylene, which, however, approaches very closely in its character to methyl-toluene or dimethyl-benzene. I do not need to enter more fully here into the further results of these interesting researches, as they were only obtained subsequent to the publication of Kekulé's paper, and in this paper they were partially foreseen. On the other hand, some of the results of Beilstein's researches were of fundamental importance with respect to the theoretical investigations now to be discussed. Of this character was the proof, carried out in conjunction with Reichenbach,[92] that the so-called salylic acid which was regarded as a benzene-carbonic acid, isomeric with benzoic acid,[93] was simply impure benzoic acid; and so was the fact that the chloro-benzoic acids prepared up to that period could be reduced in number to three.[94]

Benzene, as the fundamental substance in the aromatic group, attains to quite a special significance in consequence of the views of Kekulé, and the latter therefore makes a special study of its constitution. I shall deal with this matter in the next lecture.

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[88] Annalen. **137**, 129.

[89] Ibid. **131**, 303.

[90] Ibid. **136**, 303, etc

[91] Ann. Chim. [3] **44**, 275.

[92] Annalen. **132**, 309.

[93] Kolbe and Lautemann, ibid. **115**, 183; Kekulé, ibid. **117**, 158; Griess, ibid. **117**, 34; Cannizzaro, ibid. Supplementband **1**, 274.

[94] Beilstein and Schlun, ibid. **133**, 239.

LECTURE XIV.

THEORY OF THE AROMATIC COMPOUNDS—DETERMINATION OF POSITION OF SUBSTITUTED ATOMS OR GROUPS—QUINONES—ARTIFICIAL DYES—RING COMPOUNDS — CONSTITUTION OF THE ALKALOIDS—SYNTHESES—CONDENSATION PROCESSES.

TAKING the quadrivalence of carbon as his starting-point, Kekulé points out that in the fatty compounds the carbon atoms are linked together by one valency of each.[1] In the case of benzene, the next simplest assumption is made, in accordance with which the carbon atoms are linked together by one and by two valencies alternately, so as to form a closed chain or ring. Of the twenty-four affinities of the six carbon atoms, eighteen are employed in linking carbon to carbon, thus:—

$$\frac{6}{2}.4 + \frac{6}{2}.2 = 18$$

Six valencies then remain which are satisfied by the six hydrogen atoms of the benzene. Hence, according to Kekulé, benzene may be represented by means of a regular hexagon whose sides are composed of single and of double lines alternately, the CH groups occupying the corners.

This conception is designed to illustrate, in the first place, the relatively great stability of benzene as compared with the hydrocarbons of the fatty series, which consist of open carbon chains with, for the most part, singly linked carbon atoms. It further illustrates the fact, which is of such great importance with respect to the aromatic compounds, that the six hydrogen atoms of benzene are symmetrically disposed in the molecule—that is, that they are identical in function.

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[1] Bull. Soc. Chim. [2] **3**, 104; Annalen. **137**, 129; Lehrbuch der organischen Chemie. **2**, 493.

The aromatic compounds are obtained by the replacement of these hydrogen atoms in benzene. But it follows from the equivalence of all six hydrogen atoms that when only one of them is replaced, it must be a matter of indifference which of them it is; or, in other words, only one variety of any of the mono-substitution products of benzene can exist. A view of this kind was only possible after it had been shown that methyl-benzene is identical with toluene, and benzoic acid with salylic acid (compare p. 271).

When two or more hydrogen atoms in benzene are replaced, Kekulé's hypothesis predicts the existence of numerous isomers, occasioned by differences in the relative positions of the atoms or groups that enter the molecule; and the number of these isomers can be determined. Thus there are three isomers possible when two hydrogen atoms in benzene are replaced by other atoms or by radicals; and it is immaterial whether the atoms or radicals which enter are identical or different. Of tri-substitution derivatives of benzene there are three possible isomeric forms when the three substituting atoms or groups are the same, but six when two of them are different from the third. Further, the hypothesis foretells the existence of three isomeric tetra-substituted benzene derivatives but only one penta- and one hexa-substituted derivative when all the substituting atoms or groups, in each case, are the same. In accordance with the hypothesis, by the replacement of one or more of the hydrogen atoms in benzene by any given element or group of atoms, twelve substances can be obtained, and this has been actually accomplished in at least one case. Thus Beilstein was able to show that exactly twelve chlorinated benzenes exist,[2] after it had been proved that the alleged existence of two isomeric pentachlorobenzenes[3] was a mistake.

It follows, moreover, from the constitution of benzene, that ethylbenzene must be different from the three possible dimethylbenzenes; and, further, that by the action of chlorine or of bromine two different classes of substitution products should be obtainable from toluene, these classes being characterised by the fact that in the one the halogen replaces a hydrogen atom of the benzene (nucleus), and in the other a hydrogen atom of the methyl (side-chain). Differences of this kind were actually observed,[4] and Beilstein[5] showed that substances belonging either to the one class or to the other are produced according to whether chlorine acts in the cold or at the boiling temperature. The members of the first of these groups of chlorine compounds (of which, as di-substitution products of benzene, three isomers exist) do not permit any exchange of their chlorine for iodine, for cyanogen, or for hydroxyl or other groups containing oxygen; whereas the chlorine derivative of the other group (which, as a mono-substitution product is the only chlorine representative of the group) behaves like the chloride of an alcohol radical, and can be converted, just as easily as chlorides of this kind can, into an alcohol, an ether, etc.

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[2] Beilstein and Kurbatow, Annalen. **192**, 228. [3] Ladenburg, ibid. **172**, 331.

The two formulæ—

$C_6H_4Cl(CH_3)$	$C_6H_5CH_2Cl$
Chlorotoluenes.	Benzyl chloride.

indicate these differences, which arise, according to Kekulé, from the fact that the chlorine atom of the chlorotoluenes stands in intimate relation to the carbon (being almost entirely surrounded by it), whereas in benzyl chloride it is combined in a manner similar to the halogen of the alkyl chlorides. An explanation of an exactly similar kind is now furnished for the essentially different behaviour of the phenols and of the aromatic alcohols. Whereas in the former the hydroxyl group replaces a hydrogen atom of benzene, in benzyl alcohol the replaced hydrogen belongs to the methyl group:—

$C_6H_4(OH)CH_3$	$C_6H_5CH_2OH$
Cresols.	Benzyl alcohol.

On oxidation, the latter alone behaves as a primary alcohol and yields an aldehyde and an acid, whilst the ethers of the former are converted into alkyl-oxybenzoic acids $C_6H_4(OR)CO_2H$.[6]

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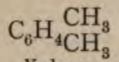
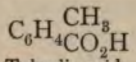
[4] Fittig, Annalen. **136**, 301; Kekulé, ibid. **137**, 192.

[5] Beilstein and Geitner, ibid. **139**, 331.

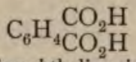
Kekulé's views concerning the oxidation of aromatic hydrocarbons into acids are very important. "It may be said in general that the alcohol residues (methyl, ethyl, etc.) attached as side-chains to the nucleus C_6 are converted, by sufficiently vigorous oxidation, into the group CO_2H. The oxidation products always contain, therefore, just as many side-chains as the substances from which they have been produced. . . . When the reactions are more moderate it is possible, in the case of those derivatives of benzene which contain two or more alcohol radicals, to restrict the action to the formation of intermediate products; thus, one alcohol radical only is oxidised in the first place, while the other remains unchanged. Dimethylbenzene (xylene) in this way yields toluylic acid. . . . On more vigorous oxidation the toluylic acid is then converted into terephthalic acid."


$C_6H_4\begin{matrix}CH_3\\CH_3\end{matrix}$

Xylene.


$C_6H_4\begin{matrix}CH_3\\CO_2H\end{matrix}$

Toluylic acid.


$C_6H_4\begin{matrix}CO_2H\\CO_2H\end{matrix}$

Terephthalic acid.

It is worth while pointing out, lastly, that Kekulé in the further elaboration of his views, cleared up the constitution of the azo-compounds[7] discovered by Mitscherlich, and, more particularly, that of the diazo-compounds discovered and minutely investigated by Griess;[8] besides showing the connection existing between these groups.[9]

These researches upon the aromatic compounds exercised an immense influence upon chemistry. The investigation of these substances, which, up to that period, had been rather neglected, was by many chemists almost exclusively worked at during the succeeding ten years. The countless examples of isomerism which previously rendered this branch so difficult to investigate (since it was only possible for a few persons to obtain a real grasp of the facts) increased the attractiveness of the investigations, now that a simple explanation of these phenomena was forthcoming. And, what is of the greatest importance, Kekulé's views were confirmed by them in the most complete manner, and did not require alteration in any essential particulars—isolated statements at variance with them always proving capable of very early refutation as incorrect. Moreover, these hypotheses were widened to a considerable extent and perfected, as a consequence of the immense number of facts afterwards discovered.

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[6] Körner, Zeitschrift für Chemie. **11**, 326. [7] Annalen. **12**, 311. [8] Ibid. **106**, 123; **109**, 286; **113**, 334; **117**, 1; Supplementband **1**, 100; **121**, 257, etc.; compare also Phil. Trans. 1864, 667, etc. [9] Lehrbuch. **2**, 703.

The problem of determining the positions of the substituting atoms and groups deserves to be mentioned here first. Merely referred to by Kekulé,[10] it was fully solved afterwards.

By determining the position in the aromatic series, we understand the ascertaining of the relations to one another and to the carbon nucleus of the atoms or groups which replace the hydrogen in benzene. Obviously the question can, at the earliest, only possess any significance in the case of the di-substitution products. The three isomers here possible, according to Kekulé, have had the distinguishing prefixes, ortho-, meta- and para- attached to their names, and the question at once arises how these are to be conceived as regards their constitution. The first step in this connection was taken by Baeyer,[11] after it had been proved by Fittig[12] that mesitylene is a trimethylbenzene. From the mode of its formation, Baeyer draws the conclusion that the three methyl groups are symmetrically arranged with respect to the benzene nucleus; that is to say, that mesitylene and isophthalic acid are meta-compounds. This hypothesis was afterwards proved[13] by an accurate investigation of the substitution products of mesitylene. Gräbe was then able to show by detailed discussions and experiments as to the nature of naphthalene[14] that this substance and, consequently, phthalic acid also, must be regarded as ortho-compounds. Finally, it was pointed out by Ladenburg,[15] taking into account the experiments of Hübner and Petermann,[16] that terephthalic acid and para-oxybenzoic acid belong to the para-series. A very neat and original idea with respect to the solution of this problem originated with Körner,[17] who showed that, by the introduction of a third atomic group into the di-substitution products containing two similar substituting atoms or groups, three isomeric tri-substitution products are possible when the original substance belongs to the meta-series, or two when it is an ortho-compound, while in the case of a para-derivative, only a single tri-substitution product is possible. By employing this method he determined the constitution of the dibromo-benzenes, and Griess[18] determined that of the phenylene diamines.

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[10] Annalen. **137**, 174. [11] Ibid. **140**, 306. [12] Zeitschrift für Chemie. **9**, 518. [13] Ladenburg, Annalen. **179**, 163. [14] Ibid. **149**, 22.

After the constitution had thus been determined in some compounds, it was still necessary to establish the relations between these and other compounds by means of simple reactions, so as to have the problem solved in the cases of all the doubly substituted benzenes. Not only has this been quite possible, but the position of the substituting groups has also been ascertained in the higher substitution products. In the whole of these often very extensive investigations, which were only practicable by the co-operation of many hands, the reactions of Griess (see above) rendered very important services.

It is likewise of considerable importance for the theory of aromatic compounds that, starting from the quadrivalence of carbon and a series of accurately determined facts, it has proved possible to establish the two fundamental principles as to the constitution of benzene, as follow:—1. The equivalence of the hydrogen atoms of benzene; and 2. The symmetry of two pairs of hydrogen atoms in benzene, with respect to the third pair of hydrogen atoms.[19]

It must further be pointed out here that a prolonged controversy arose concerning the formula of benzene (that is, as to the mutual linkings of the carbon atoms which it contains) after attention had been drawn to the fact that Kekulé's formula does not altogether take account of the requirements involved in the two principles stated above.[20] From this controversy it appeared that only the so-called prism formula can give a clear idea of the bearings of isomerism in the aromatic series, since it furnishes likewise an accurate expression for the thermal relations, according to Thomsen, and for the molecular volume of benzene and its derivatives, according to R. Schiff.[21] Nevertheless Kekulé's hexagon formula has been generally retained, because it is superior to the other formula in many respects.

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[15] Berichte. **2**, 140.

[16] Annalen. **149**, 129.

[17] Gazzetta Chimica Italiana. **4**, 305; Journ. Chem. Soc. **29**, 204.

[18] Berichte. **7**, 1226.

[19] Ladenburg, Theorie der aromatischen Verbindungen, Braunschweig 1876; Berichte. **10**, 1224; Wroblewsky, Annalen. **192**, 196.

Amongst the notable researches which were instigated by Kekulé's investigations, I only enter into detail here respecting a single one which may probably be looked upon as the most important amongst them. I refer to Gräbe's examination of the quinones.

Kekulé propounded a peculiar view respecting quinone,[22] a substance which had been discovered by Woskresensky.[23] This substance was supposed to consist of an open chain of six carbon atoms, which were joined to one another by single and double linking alternately. In opposition to this view Gräbe[24] advanced another, in accordance with which quinone is a benzene derivative in which two hydrogen atoms are replaced by two oxygen atoms; and these latter are further united to each other. He bases this view especially upon the already well-known relations of quinone to hydroquinone, and upon the conversion of chloranil into hexachlorobenzene by means of phosphorus pentachloride. These grounds were so convincing that Gräbe's view was generally adopted, even although it appeared soon after that quinone did not belong to the ortho-compounds, as Gräbe supposed, but to the para-compounds.[25] Gräbe afterwards studied other quinones also, and so arrived at the investigation of alizarine, the nature of which as a quinone he desired to establish. In conjunction with Liebermann, and by making use of a method discovered by Baeyer,[26] he showed that alizarine was not, as was then supposed, a naphthalene derivative, but that it was derived from anthracene;[27] that it was a quinone; and that, in particular, it was a dioxy-anthraquinone. These chemists afterwards accomplished the synthesis of this valuable colouring matter,[28] which was at once prepared technically according to a method elaborated by Gräbe, Liebermann, and Caro;[29] thus leading to one of the most extensive industries of the present time.

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[20] Ladenburg, Berichte. **2**, 140. [21] Ibid. **13**, 1808; see also Thomsen, Thermochemische Untersuchungen. 4; also Schiff, Annalen. **220**, 303. According to Schröder (Wiedem. Ann. **15**, 667) this also holds for the molecular refraction; whereas, according to Brühl (Annalen. **200**, 229), the opposite is the case. [22] Annalen. **137**, 134. [23] Ibid. **27**, 268. [24] Ibid. **146**, 1.

It may be stated generally that the theory of the aromatic compounds had a great influence in technology and especially in that of dyes. Although the aniline colour industry was called into existence quite independently of these investigations (especially by Hofmann's comprehensive researches on aniline, and the bases homologous with it), and although the first aniline colours had been discovered and turned to account long prior to the publication of Kekulé's celebrated paper—mauveïne by Perkin[30] as early as 1856, and fuchsine by Verguin[31] in 1859, after it had been previously observed by Natanson,[32] Hofmann,[33] and others—still its further development is intimately connected with the more accurate insight into the constitution of the aromatic compounds. With respect to this, it is only necessary to recall the discovery of orthotoluidine by Rosenstiehl,[34] and the explanation of the chemical nature of rosaniline, which was eventually furnished by E. and O. Fischer,[35] the way having been prepared by Hofmann.[36]

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[25] Petersen, Berichte. **6**, 368 and 400.

[26] Annalen. **140**, 295.

[27] Berichte. **1**, 49.

[28] Annalen. Supplementband **7**, 257; Berichte. **2**, 14.

[29] Ibid. **3**, 359.

[30] Perkin, Zeitschrift für Chemie. **4**, 700; Annalen. **131**, 201.

[31] Répert. de Chimie appliquée. **2**, 114, 299; compare also Dingl. Polyt. Journ. **154**, 235, 397.

[32] Annalen. **98**, 297.

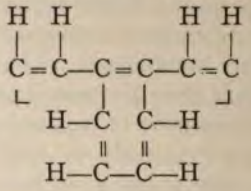
[33] Jahresbericht 1858, 351.

[34] Zeitschrift für Chemie. **11**, 557; **12**, 189-190.

The manufacture of other classes of dyes has also arisen independently of this theory, although no doubt advanced by means of it. Examples of these substances are the phenol dyes, of which the first representative is rosolic acid, discovered by Kolbe and Schmitt[37] and simultaneously by J. Persoz;[38] and this group was greatly enlarged by the phthaleïnes, discovered and studied by Baeyer.[39] Other examples are the azo-dyes, which are, almost without exception, connected with the important researches of Griess.

The influence which Kekulé's conception of the aromatic compounds exercised upon the views concerning the more complicated hydrocarbons is much more direct.

Erlenmeyer,[40] in an interesting paper on aromatic acids, which contains a criticism of Kekulé's views, assigns to naphthalene, $C_{10}H_8$, the formula:—



In accordance with this formula, naphthalene could be conceived as composed of two benzene hexagons with two carbon atoms common to both of them. Gräbe rendered this conception very probable by means of experimental investigations and theoretical considerations.[41] Aronheim's synthesis of naphthalene from phenyl butylene[42] also tells in support of it, and so, especially, does Fittig's synthesis of *a*-naphthol[43] (the hexagon formula for benzene being assumed). This view concerning naphthalene leads to the assumption of two isomeric mono-substitution products. Faraday had, in fact, prepared two naphthalene mono-sulphonic acids,[44] and many similar cases have been observed since then. It has even proved possible in the cases of naphthalene derivatives to carry out determinations of the positions of the atoms with a very high degree of probability; and here, also, after a detailed study of the naphthalene series, a marked agreement between fact and theory is observed.[45]

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[35] Annalen. **194**, 242.

[36] J. pr. Chem. **87**, 226; Jahresbericht 1863, 417; 1864, 819; Annalen. **132**, 160 and 289.

[37] Ibid. **119**, 169.

[38] French Patent, 21st July 1862.

[39] Annalen. **183**, 1; **202**, 36.

[40] Ibid. **137**, 327.

[41] Ibid. **149**, 1.

[42] Ibid. **171**, 233.

[43] Fittig and Erdmann, Berichte. **16**, 43; Annalen. **227**, 242.

Anthracene, the starting-point in the preparation of so many interesting compounds and valuable dyes, was early recognised as a closed carbon chain, and as "a nucleus derivable from benzene." Gräbe and Liebermann,[46] in their first communication on the connection between alizarine and anthracene, proposed a formula for the latter, in accordance with which it is represented as tribenzene; that is, as made up from three molecules of benzene and as having four of its carbon atoms common to two different hexagons. Besides this, in their detailed paper, they afterwards advanced another similar formula for anthracene, which, however, seemed to them to be less probable. After the discovery of phenanthrene (which is isomeric with anthracene) and the special study of it, for which we are indebted to the almost simultaneous investigations of Gräbe and Glaser[47] and of Fittig and Ostermeyer,[48] the first anthracene formula was recognised as representing phenanthrene and the second one was retained for anthracene. The latter formula meets all requirements, and this is a matter which is really astonishing, in view of the numerous isomerisms in the anthracene group. It is also capable of giving a clear representation of the neat syntheses of anthraquinone, alizarine, quinizarine, and purpurine, effected by

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[44] Phil. Trans. 1826, 140; Ann. Chim. [2] 34, 164.

[45] Compare especially Reverdin and Nölting, Ueber die Constitution des Naphtalins, Genf 1880; also Liebermann and Dittler, Annalen. 183, 228.

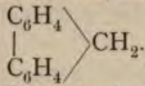
[46] Berichte. 1, 49.

[47] Ibid. 5, 861 and 968; Annalen. 167, 131.

[48] Berichte. 5, 933; Annalen. 166, 361; compare also Hayduck, ibid. 167, 177.

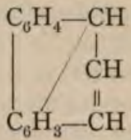
Kekulé and Franchimont,[49] by Baeyer and Caro,[50] and by Piccard,[51] since it brings out plainly the relations between phthalic anhydride and anthraquinone.

Further, the constitutions of fluorene, fluoranthene, chrysene, and retene, as well as their relations to benzene, are now cleared up. Fluorene, $C_{13}H_{10}$, discovered by Berthelot,[52] is obtained by Fittig[53] by the distillation of diphenylketone with zinc dust, and is thus recognised as diphenylene methane,

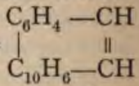


$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right\rangle CH_2$.

Fluoranthene (idryl), $C_{15}H_{10}$, isolated by Goldschmiedt[54] from a semi-solid by-product obtained during the distillation of the ores of mercury at Idria, and also occurring in coal tar,[55] is probably represented by the formula—

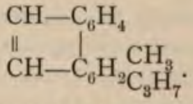


Chrysene, $C_{18}H_{12}$, is recognised, from a synthesis of it effected by Gräbe,[56] as a naphthalene-phenanthrene



$$\begin{array}{lcl}C_6H_4 & — & CH\\ | & & \|\\ C_{10}H_6 & — & CH\end{array}$$

that is to say, as phenanthrene in which one of the phenylene groups is replaced by a naphthalene group. Finally, retene, $C_{18}H_{18}$, according to the investigations of Bamberger and Hooker,[57] is a methyl-propyl-phenanthrene—



$$\begin{array}{lcl}CH & — & C_6H_4\\ \| & & |\\ CH & — & C_6H_2{\begin{array}{l}CH_3\\ C_3H_7\end{array}}\end{array}.$$

Hence, it can scarcely be doubted that the other hydrocarbons with high molecular weights, which are not so fully examined as yet (such as pyrene, picene, etc.), may be derived from benzene in an analogous manner.

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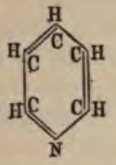
[49] Berichte. **5**, 908. [50] Ibid. **7**, 972; **8**, 152. [51] Ibid. **7**, 1785.

[52] Annalen. Supplementband **5**, 371. [53] Berichte. **6**, 187; Annalen. **193**, 134. [54] Berichte. **10**, 2022. [55] Fittig and Gebhard, ibid. **10**, 2143; Annalen. **193**, 142; Fittig and Liepmann, ibid. **200**, 1.

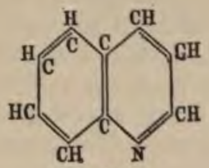
[56] Berichte. **12**, 1078. [57] Ibid. **18**, 1024 and 1750; Annalen. **229**, 102.

Some other investigations in which a relationship can be recognised between certain compounds containing nitrogen—especially the alkaloids—and benzene, appear to be probably still more important than the foregoing. This branch of the subject, only opened up a few years ago, already presents so many remarkable results that it cannot be omitted here.

The analogy of the formulæ of benzene, C_6H_6, and naphthalene $C_{10}H_8$, on the one hand, with those of pyridine, C_5H_5N, and quinoline, C_9H_7N, on the other, admitted of the hypothesis that the latter compounds might be derived from the former by the replacement in each of a CH group by N, and consequently the following formulæ were advanced for pyridine and quinoline.



Pyridine.



Quinoline.

This view was made known by means of private communications by Körner, and is usually known as Körner's hypothesis. It was first published by Dewar.[58]

A large number of facts can now be adduced in support of the view, and the more important of these may be mentioned here.

Anderson, the discoverer of pyridine, had already found in animal oil, besides pyridine, a number of homologous bases.[59] The further examination of bone tar has yielded, as yet, only methyl pyridines,[60] just as methyl benzenes only are contained in coal tar. Ethyl and propyl pyridines are already known, however.[61] On oxidation, these bases behave exactly like the alkyl derivatives of benzene; that is to say, every side-chain, by sufficiently energetic oxidation, yields a CO_2H group; so that, in this case also, conclusions may be drawn as to the number of side-chains in the base oxidised, from the basicity of the acid produced.

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[58] Chem. News. **23**, 38 ; Zeitschrift für Chemie. **14**, 117.

[59] Annalen. **60**, 86 ; **70**, 32 ; **75**, 80 ; **80**, 44 : **94**, 358 ; see also Unverdorben, Pogg. Ann. **11**, 59.

[60] Weidel, Berichte. **12**, 1989 ; Ladenburg and Roth, ibid. **18**, 47 and 913.

The isomerisms amongst the derivatives of pyridine are far more complicated that in those of benzene, since the hydrogen atoms are not similarly related to the pyridine nucleus and three different mono-substitution products must exist, as was probably first pointed out by Weidel.[62] This conclusion is likewise confirmed by experiment, as three mono-carbonic acids,[63] three methyl-pyridines[64] and three ethyl-pyridines[65] are known. Determinations of the positions of the substituting atoms or groups in the pyridine series have been accomplished with tolerable certainty by Skraup.[66]

As additional supports for the pyridine formula, there may also be adduced the synthesis of pyridine by Ramsay[67] (which is upon the same lines as the famous synthesis of benzene from acetylene by Berthelot[68]) as well as the syntheses of pyridine derivatives.[69] Finally the conversion of pyridine derivatives into benzene derivatives[70] is of importance in this connection.

The formula for quinoline is also based upon numerous syntheses, of which that by Königs[71] may be mentioned here as the first. This was followed by that of Baeyer[72] and then by the one of Skraup [73] which has become so important for the whole group. This latter synthesis depends upon the carrying out of one of the ideas indicated by Gräbe.[74]

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[61] Williams, Jahresbericht 1855, 549; 1864, **437**; Cahours and Etard, Comptes Rendus. **92**, 1079; Ladenburg, Berichte, **16**, 2059; **17**, 772 and 1121; **18**, 1587; Hofmann, ibid. **17**, 825.

[62] Ibid. **12**, 2012.

[63] Huber, Annalen. **141**, 271; Berichte. **3**, 849; Weidel, ibid. **12**, 1989; Skraup, ibid. **12**, 2331.

[64] Weidel, ibid. **12**, 1989; Behrmann and Hofmann, ibid. **17**, 2681.

[65] Wischnegradsky, ibid. **12**, 1480; Ladenburg, ibid. **16**, 2059.

[66] Skraup and Cobenzl, Monatshefte. **4**, 450; compare also Ladenburg, Berichte, **18**, 2967.

[67] Ibid. **10**, 736.

[68] Ann. Chim. [4] **9**, 469.

[69] Hantzsch, Annalen. **215**, 1; Pechmann and Welsh, Berichte. **17**, 2384; Behrmann and Hofmann, ibid. **17**, 2681.

[70] Ladenburg, ibid. **16**, 2059.

[71] Ibid. **12**, 453.

[72] Ibid. **12**, 460.

Quinoline, also, is the starting-point for a large number of compounds, which are formed from it and can be converted into it just as benzene passes into aromatic compounds and can be obtained from them.

The relations between pyridine and quinoline, which are quite analogous to those between benzene and naphthalene, are also worthy of mention. In the same way that the latter is converted by oxidation into benzene-ortho-dicarbonic acid (phthalic acid [75]), so quinoline, according to Hoogewerff and Van Dorp,[76] is converted by oxidation into an ortho- ($\alpha\beta$-) pyridine-dicarbonic acid.

But what is of the greatest significance is the fact that the most important alkaloids are derivatives of pyridine and of quinoline (or of their hydrogenised derivatives) in the same way that the aromatic oils are derivates of benzene. The first fact bearing upon this relationship was found out by Gerhardt in 1842, when he discovered quinoline as a product of the decomposition of quinine, of cinchonine, and of strychnine.[77] Huber obtained in 1867, by the oxidation of nicotine,[78] an acid $C_6H_5NO_2$ which he recognised, three years later, as pyridine-carbonic acid [79]—a fact which was at first disputed and then confirmed.[80] Piperidine, which was discovered by Wertheim and Rochleder by the decomposition of piperine,[81] and the correct formula of which was established by Cahours [82] and by Anderson,[83] was regarded by Hofmann as a hydrogen addition product of pyridine,[84] a view which was proved to be correct by Königs and others.[85]

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[73] Monatshefte. **1**, 317; **2**, 141.

[74] Annalen. **201**, 333.

[75] Laurent, ibid. **19**, 38; **41**, 98.

[76] Berichte. **12**, 747.

[77] Annalen. **42**, 310; **44**, 279.

[78] Ibid. **141**, 271.

[79] Berichte. **3**, 849.

[80] Weidel, Annalen. **145**, 328; and Laiblin, ibid. **196**, 129.

[81] Ibid. **54**, 254; **70**, 58.

[82] Ibid. **84**, 342.

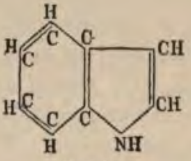
[83] Ibid. **84**, 345.

[84] Berichte. **12**, 984.

[85] Ibid. **12**, 2341; Schotten, ibid. **15**, 421; Hofmann, ibid. **16**, 586; Ladenburg, ibid. **17**, 156, 388; Ladenburg and Roth. **17**, 513.

These and other facts, which seemed to place beyond doubt the relations of several natural bases to pyridine,[86] led Wischnegradsky to the opinion stated above regarding the constitution of the alkaloids;[87] and this was more fully discussed and established, a year later, by Königs.[88] Since then, this view has gained ground more and more; especially as a series of facts have been discovered in support of it. Thus Weidel obtained a pyridine-tricarbonic acid by the oxidation of berberine;[89] Gerichten was able to prepare pyridine-dicarbonic acid from narcotine,[90] and Ladenburg dibromo-pyridine from atropine;[91] while Hofmann converted coniine into propyl-pyridine.[92]

The results which attended this view of pyridine and of quinoline, and the recognition which they met with, led to the introduction of a similar view concerning many other substances. In the first place it is necessary to consider the formula which was assigned as early as 1869, by Baeyer and Emmerling,[93] to indol,[94] the starting-point for most of the indigo derivatives:—



Indol.

According to this formula indol is represented as a double nucleus resembling naphthalene and quinoline. This mode of representing it acquired greater significance when Baeyer and Emmerling,[95] somewhat later, regarded pyrrol also as a "ring." The same relation was now assumed between pyrrol and indol as between pyridine and quinoline or between benzene and naphthalene:

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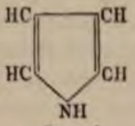
[86] Weidel, Annalen. 173, 76; Ramsay and Dobbie, Berichte. 11, 324.
[87] Ibid. 12, 1506; compare also Ladenburg, ibid. 12, 947.
[88] Studien über die Alkaloide, Munich 1880.
[89] Berichte. 12, 410.
[90] Annalen. 210, 101.
[91] Ibid. 217, 148.
[92] Berichte. 17, 825.
[93] Ibid. 2, 679.
[94] Baeyer, ibid. 1, 17.
[95] Ibid. 3, 517.



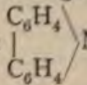
Pyrrol.

The analogues are:—

C_6H_6 Benzene.	$C_{10}H_8$ Naphthalene.
C_5H_5N Pyridine.	C_9H_7N Quinoline.
C_4H_5N Pyrrol.	C_8H_7N Indol.

At the same time, tetra-phenol[96] (furfuran), C_4H_4O, discovered by Limpricht, was represented by a formula analogous to that for pyrrol, the NH group of the latter being regarded as replaced by O. Related to furfuran, there is thiophen, C_4H_4S,[97] (discovered more recently by V. Meyer), which is looked upon as thiofurfuran, and which has already become of great importance on account of its numerous derivatives. In the case of thiophen the resemblance exhibited by it and its derivatives to benzene and the benzene derivatives is particularly noteworthy.

Carbazol,[98] discovered by Fritzsche, may also be mentioned here—a substance which Gräbe[99] regards as fluorene in which CH_2 is replaced by NH, thus:


$\left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right\rangle NH$

Further, there is acridine,[100] found in crude anthracene by Gräbe and Caro, which is regarded as a derivative of anthracene[101] or of phenanthrene[102] in which an atom of nitrogen has taken the place of CH.

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[96] Berichte. 3, 90. [97] Ibid. 16, 1465. [98] J. pr. Chem. 73, 286; 101, 342. [99] Annalen. 167, 125, 174, 180. [100] Ibid. 158, 265. [101] Riedel Berichte. 16, 1609; Bernthsen and Bender, ibid. 16, 1803.

I have already stated (p. 117) that all these investigations as to the constitution of organic compounds were occasioned by the numerous cases of isomerism which meet the chemist at almost every step, and the existence of which seems to require some explanation. It must be acknowledged, that the theory of the valency or atomicity of the elements fulfilled this requirement to a large extent, and in this lies the great importance of that theory; whereas, on the other hand, it cannot be denied that the principles of the theory are far from being clearly and precisely worked out—a matter into which I intend to enter more fully in the next lecture. But attention may here be called to the fact that not merely is the possibility of an explanation of these isomerisms supplied to us by the advancement of our theoretical knowledge, but this explanation chiefly depends upon the much more extensive experimental material at our disposal. And this material has, in great part, been obtained by the application of a method which, even although it has been recognised for a long time as a possible one, has only attained to pre-eminent importance within comparatively recent times. I refer to the method of synthesis, which is, moreover, in many cases, not merely a means to an end, but is itself the aim of the experiments.

In an earlier lecture (p. 116) the synthesis by Wöhler of an organic compound (urea) was mentioned, and also the importance of this synthesis in regard to our whole conception of nature. Similar results were only obtained in the cases of other substances long afterwards, and the value of this method was shown in a proper light by Berthelot's comprehensive work.[103] The syntheses of some specially important substances—marsh gas, ethylene, alcohol, formic acid, benzene, etc.—also originated with Berthelot.

It has been found in many cases that the earlier analytical method is not sufficient for establishing the chemical nature of a compound, and that the synthetical method constitutes a necessary complement. The first method usually precedes the second; but, in the history of a substance, its synthesis, with rare exceptions, marks a period, and, with it, the interest which the scientific investigation of the substance presents is usually at an end.

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[102] Ladenburg, Berichte. **16**, 2063; Gräbe, ibid. **17**, 1370.

[103] Chimie organique fondée sur la Synthèse, Paris 1860.

From this point of view, the syntheses of specially important substances are worthy of mention here. Thus alanine was prepared, in 1850, by Strecker, from aldehyde-ammonia, hydrocyanic acid, and hydrochloric acid.[104] Five years later, Zinin obtained mustard oil from allyl iodide and potassium thiocyanate,[105] its connection with garlic oil having already been established much earlier by Wertheim.[106] Glycocoll was prepared synthetically by Perkin and Duppa[107] from bromacetic acid and ammonia, and Hüfner afterwards obtained leucine[108] in an analogous manner. Racemic acid was prepared synthetically by Perkin and Duppa[109] from dibromsuccinic acid, and malic acid by Kekulé[110] from monobromsuccinic acid. We are indebted to Kolbe for the synthesis of taurine,[111] a substance which he prepared from isethionic acid. Anthracene was first prepared artificially by Limpricht, by boiling benzyl chloride with water;[112] and guanidine was prepared by Hofmann,[113] who obtained it from chlorpicrin, and by Erlenmeyer,[114] who obtained it from cyanamide by the action of ammonia. Volhard prepared creatine synthetically from chloracetic acid,[115] by converting the latter into sarcosine by the action of methylamine and then converting the sarcosine into creatine by means of cyanamide. Picoline and collidine were prepared synthetically by Baeyer[116] from aldehyde-ammonias; crotonic acid, by Kekulé, from aldehyde;[117] and glycerine by Friedel and Silva, starting from acetone.[118] Wurtz[119] converted glycol chlorhydrine into choline (neurine) by means of trimethylamine, whilst Reimer and Tiemann obtained vanilline from guaiacol.[120] Grimaux synthetically prepared allantoïn,[121] alloxantine,[122] and citric acid;[123] and, more recently, Erlenmeyer prepared tyrosine,[124] Ladenburg, piperidine[125] and coniine,[126] and Horbaczewsky, uric acid.[127] The synthesis of indigo blue by Baeyer[128] also deserves to be mentioned, since not only did it familiarise us with the preparation and furnish us with an explanation of the constitution of an important colouring matter, but it was accomplished, besides, by means of new and peculiar reactions.

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[104] Annalen. **75**, 29. [105] Ibid. **95**, 128. [106] Ibid. **55**, 297. [107] Ibid. **108**, 112. [108] Hüfner, J. pr. Chem. [2] **1**, 6. [109] Journ. Chem. Soc. **13**, 102; Annalen. **117**, 130. [110] Ibid. **117**, 120. [111] Kolbe, ibid. **122**, 33. [112] Ibid. **139**, 308. [113] Berichte. **1**, 145. [114] Annalen. **146**, 259. [115] Zeitschrift für Chemie. **12**, 318. [116] Annalen. **155**, 283. [117] Ibid. **162**, 92.

Special attention is due to the general methods which permit the synthesis of whole groups of substances. The most important of these methods will be specified here.

Frankland was the first who succeeded in building up hydrocarbons.[129] He obtained dimethyl (ethane) from zinc and methyl iodide, and diethyl (butane) from zinc and ethyl iodide. This reaction was extended by Wurtz, who treated mixtures of alkyl iodides with sodium[130]—a method which Fittig and Tollens turned to account in the synthesis of aromatic hydrocarbons.[131] It had already been found possible to obtain hydrocarbons, according to a reaction discovered by Berthelot, by the distillation of benzoates with salts of the fatty acids.[132] A synthetical method was elaborated by Zincke, which permits of the preparation of hydrocarbons with two phenyl groups, and depends upon the action of benzyl chloride upon aromatic hydrocarbons in presence of zinc dust.[133] These compounds can also be obtained, according to Baeyer, from aldehydes and aromatic hydrocarbons, by the aid of substances which remove the elements of water.[134] A method of very general applicability is that discovered by Friedel and Crafts,[135] which renders it possible, by the help of aluminium chloride, to introduce groups of very different kinds into an aromatic substance, with simultaneous separation of hydrochloric acid or of water, and thus permits the synthesis of hydrocarbons, ketones, acids, etc.

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[118] Bull. Soc. Chim. [2] **20**, 98.

[119] Annalen. Supplementband **6**, 116.

[120] Berichte. **9**, 424.

[121] Ann. Chim. [5] **11**, 389.

[122] Jahresbericht **1878**, 361.

[123] Comptes Rendus. **90**, 1252.

[124] Annalen. **219**, 161.

[125] Berichte. **18**, 2956 and 3100.

[126] Ibid. **19**, 439 and 2578.

[127] Monatshefte. **3**, 796; **6**, 356.

[128] Berichte. **13**, 2254.

[129] Annalen. **71**, 171; **74**, 41; **77**, 221.

[130] Ibid. **96**, 364.

[131] Ibid. **131**, 303.

[132] Ann. Chim. [4] **12**, 81.

[133] Annalen. **155**, 59, etc.

The possibility of ascending in the series of the primary alcohols, from one term to the next higher term, was shown by the investigations of Pelouze,[136] Kolbe and Frankland,[137] Piria,[138] and Wurtz.[139] The desired end is attained by the conversion of the alcohol into cyanide, acid, aldehyde, and alcohol, in accordance with the following equations :—

$$\begin{aligned}
CNK + C_2H_5SO_4K &= C_2H_5CN + SO_4K_2 \\
C_2H_5CN + KOH + H_2O &= C_2H_5CO_2K + NH_3 \\
C_2H_5CO_2K + CHO_2K &= C_2H_5COH + CO_3K_2 \\
C_2H_5COH + H_2 &= C_2H_5CH_2OH.
\end{aligned}$$

Lieben and Rossi ascertained the general applicability of the methods.[140] There is also a second mode for obtaining, from one alcohol, the next term in the homologous series, viz., by converting the cyanide (nitrile) into an amine by means of nascent hydrogen (Mendius[141]), and then decomposing this by means of nitrous acid (Hunt[142]). A statement has already been made about the synthesis of secondary and tertiary alcohols (pp. 262 and 264). The preparation of the phenols from the hydrocarbons is accomplished by a process which Dusart, Kekulé, and Wurtz[143] announced simultaneously.

Aceto-acetic ether has become of great importance in the synthesis of acids, as already stated (p. 264). Malonic ether[144] and benzoyl-acetic ether[145] have also been made use of in a similar manner; whilst it has been possible, on the other hand, to obtain synthetically some interesting nitrogen compounds by the aid of aceto-acetic and malonic ethers.[146]

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[134] Berichte. **5**, 1094. [135] Comptes Rendus. **84**, 1392, 1450; **85**, 74, etc. [136] Annalen. **10**, 249. [137] Ibid. **65**, 288; see also Fehling, ibid. **49**, 95. [138] Ibid. **100**, 104; compare also Limpricht, ibid. **97**, 368. [139] Ibid. **123**, 140. [140] Ibid. **165**, 109. [141] Mendius, ibid. **121**, 129. [142] Liebig and Kopp's Jahresbericht 1849, 391. [143] Comptes Rendus. **64**. [144] Conrad and Bischoff, Annalen. **204**, 121. [145] Baeyer, Berichte. **15**, 2705; Baeyer and Perkin, ibid. **16**, 2128.

Perkin's reaction,[147] which is connected with observations made by Bertagnini,[148] and depends upon the action of aldehydes on the salts of organic acids in presence of agents which remove the elements of water, has led to the preparation of a large number of acids. It was first employed in a somewhat more complicated form, however, in the synthesis of cumarine.[149] The conversion of nitriles into acids, already referred to above, has also been employed in the preparation of polybasic acids; and, for this purpose, it is possible to start, as Simpson did,[150] from the cyanogen compounds of polyatomic radicals, or, as was shown by Kolbe[151] and by H. Müller,[152] from the cyanogen derivatives of acids. The first conversion of a nitrile into an acid was carried out, however, by Pelouze,[153] who, in 1831, converted hydrocyanic acid into formic acid, and who reconverted the ammonium salt of the latter into hydrocyanic acid by the action of heat. Winkler,[154] a few years afterwards, converted oil of bitter almonds containing hydrocyanic acid, into mandelic acid—a reaction which was correctly interpreted by Liebig.[155] Polybasic acids can also be obtained by a process published by Wislicenus,[156] whilst Kolbe's reaction, which consists in treating phenates with carbonic anhydride, is of great importance in the synthesis of phenol acids.[157] Related to this, there is Reimer's synthesis of phenol aldehydes from phenates and chloroform.[158]

Finally Hofmann's method for the formation of alkyl bases[159] may here be referred to. This method he afterwards altered and considerably improved.[160]

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[146] Compare especially Hantzsch, Annalen. **215**, 1; Knorr, Berichte. **17**, Referate. 148, 540, 1635 etc.; Rügheimer, ibid. **17**, 736.

[147] Ibid. **8**, 1599; compare also Fittig, Annalen. **216**, 115; **227**, 48.

[148] Ibid. **100**, 126.

[149] Ibid. **147**, 229.

[150] Ibid. **118**, 373; **121**, 153.

[151] Ibid. **131**, 348.

[152] Ibid. **131**, 350.

[153] Ann. Chim. [2] **48**, 395.

[154] Annalen. **18**, 310.

[155] Ibid. **18**, 319.

[156] Ibid. **149**, 215.

[157] Kolbe and Lautemann, ibid. **115**, 201; Kolbe, J. pr. Chem. [2] **10**, 93.

[158] Berichte. **9**. 423.

In many of these investigations an idea was turned to account which has already borne much fruit, and which will, no doubt, also be of great service in future. I refer to the so-called condensation processes; that is, to the very frequently occurring formations, both in nature and in artificial reactions, of complex substances from simple ones, where several identical or similar molecules unite to form one molecule, usually with the simultaneous elimination of hydrogen, water, ammonia, etc. Gerhardt drew attention to reactions of this kind when he formulated his theory of residues (p. 180), but it is only in comparatively recent times—within the last thirty years or thereabouts—that the necessary attention has been bestowed upon these processes. Berthelot was probably the first who closely studied such reactions, and he obtained valuable results by doing so. Amongst these results are the syntheses, discovered by him, of benzene C_6H_6 from acetylene, of diphenyl from benzene, of anthracene from toluene,[161] etc. In these experiments he established, amongst other things, the fact, which has since been frequently confirmed, that at a high temperature several molecules of a hydrocarbon may unite to form a new molecule with the elimination of hydrogen.

Some time afterwards, Baeyer began to work at this subject. He regards the difference between condensation and polymerisation as consisting in the fact that in the former the molecules combine by virtue of union with carbon atoms, and in the latter of union with oxygen or with nitrogen atoms.[162] It is already clear to him that for purposes of synthesis, condensation is alone of importance. He draws attention, besides, to very important syntheses which have already been carried out, such as the formation of mesitylene from acetone by Kane,[163] and Chiozza's synthesis of cinnamic aldehyde from bitter almond oil and aldehyde by the action of hydrochloric acid.[164] He then turns the theoretical views advanced at that time to immediate account in the synthesis of picoline and collidine, which are obtained by the condensation of acrolein-ammonia and of aldehyde-ammonia :—[165]

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[159] Annalen. **66**, 129; **67**, 61 and 129; **70**, 129; **73**, 180; **74**, 1, 33, 117; **75**, 356; **78**, 253; **79**, 11.

[160] Berichte. **14**, 2725; **15**, 407, 752, 762.

[161] Bull. Soc. Chim. [2] **6**, 268.

[162] Annalen. Supplementband **5**, 79.

[163] Ibid. **22**, 278.

$$2C_3H_4ONH_3 = C_6H_7N + 2H_2O + NH_3$$
$$4C_2H_4ONH_3 = C_8H_{11}N + 4H_2O + 3NH_3.$$

Kekulé, a few years later, condensed two molecules of aldehyde so as to form crotonic aldehyde,[166] thereby throwing light upon the chemical nature of the so-called acrylic aldehyde already examined by Lieben.[167] This reaction was afterwards studied by Wurtz,[168] who showed that the two aldehyde molecules unite in the first place, without the elimination of water, to form aldol, the aldehyde of β-hydroxybutyric acid, and that crotonic aldehyde is then formed from the latter by the loss of water. The general character of this interesting reaction was established, subsequently, by various investigations, and especially by the researches of Claisen.[169]

The idea of condensation has been greatly extended in recent times, every reaction in which union of carbon to carbon occurs amongst the molecules that act upon one another being designated a condensation. The word thus became synonymous with synthesis, and lost all independent meaning and all meaning corresponding to its etymology. It is due to this that Baeyer's reaction for the formation of hydrocarbons from aldehydes and benzene and its derivatives, and likewise Perkin's method of forming unsaturated acids from aldehydes and the salts of fatty acids, came to be designated as condensations.

The idea of condensation has also undergone change in another direction inasmuch as internal condensations have been contrasted with the processes just mentioned, which have in turn been called external condensations. By internal condensations we now understand reactions in which a single molecule of a substance becomes converted into a new molecule by parting with some of its atoms, which unite to form such a molecule as H_2, HCl, H_2O, NH_3, etc. ; *i.e.*, reactions which occur within a molecule. As applied to such reactions, the word condensation so far retains its meaning, that the atoms are related more intimately (that is, by a greater number of valencies) to one another. Amongst these reactions there are many processes which have long been known, such as the formation of ethylene from alcohol, of C_2Cl_4 from C_2Cl_6, of aldehydes or of ketones from alcohols, of ethylene oxide from glycol, of anhydrides from polybasic acids, etc. But the formation of the anhydrides of monobasic acids, of the lactones and of the lactone acids, which have been minutely studied by Fittig, comparatively recently, must also be regarded as internal condensations. To the same class of reactions belong, further, the formation of cumarine, and that of the oxycumarines (umbelliferone, daphnetine, etc.), of isatine, indol, rosaniline, of rosolic acid, of the phthaleïnes, of the aldehydines, of quinoline, naphthalene, anthracene, etc. Consequently these processes have played an important part in more recent investigations, and they will engage our attention here a little longer.

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[164] Annalen. **97**, 350. [165] Ibid. **155**, 283 and 297. [166] Ibid. **162**, 77. [167] Ibid. **106**, 336; Supplementband. **1**, 114. [168] Jahresbericht **1872**, 449; **1873**, 474; **1876**, 483; **1878**, 612. [169] Annalen. **180**, 1; ibid. **218**, 121.

The formation of ethenyl-xylene-diamine and of ethenyl-toluylene-diamine by the reduction of nitro-acet-xylid and of nitro-acet-toluid, observed by Hobrecker,[170] first attracted Hübner's attention to this matter. The latter chemist prepared a large number of analogous compounds, and was able to show that this abnormal course of the reduction only occurred with the ortho-benzene derivatives, and not with the meta- or para-derivatives.[171] This was entirely confirmed by Ladenburg's investigations.[172] The latter chemist discovered quite a number of reactions which proceed in an altogether different manner in the ortho-series from that in which they proceed in the other isomeric series. In the case of the diamines, he showed, by means of reactions of this very kind, how the ortho-compounds may be distinguished from their isomers; and he was the first to point out that the formation of the above-mentioned substances depends upon "ortho-condensation." Baeyer then turned his attention to this subject, and the syntheses of quinoline (already referred to) and of oxindol constitute the valuable fruits of his studies.

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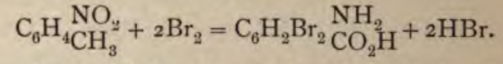
[170] Berichte. **5**, 920.

[171] Ibid. **8**, 471 ; Annalen. **208**, 278 ; **209**, 339 ; **210**, 328.

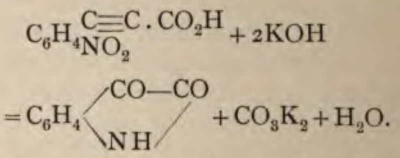
[172] Berichte. **8**, 677 ; **9**, 219 and 1524 ; **10**, 1123, 1260, etc.

Closely related to this internal condensation, is internal oxidation. Reactions involving the latter change are those in which oxygen atoms already present in the molecule, and generally belonging to NO_2 groups, oxidise, by the dissolution of existing unions, other groups belonging to the same molecule. The first reaction of this kind was observed by Wachendorff,[173] but Greiff[174] was the first to explain it. The matter involved was the action of bromine on ortho-nitrotoluene, which the latter of the above-named chemists represented in the following manner :—



$$C_6H_4\begin{matrix}NO_2\\CH_3\end{matrix} + 2Br_2 = C_6H_2Br_2\begin{matrix}NH_2\\CO_2H\end{matrix} + 2HBr.$$

This reaction furnishes the explanation of the important method, discovered by Baeyer,[175] for preparing isatine from ortho-nitro-phenylpropiolic acid, by boiling this acid with alkalies :—



$$C_6H_4\begin{matrix}C\equiv C\,.\,CO_2H\\NO_2\end{matrix} + 2KOH$$

$$= C_6H_4\begin{matrix}CO-CO\\NH\end{matrix} + CO_3K_2 + H_2O.$$

The formation of indigo from ortho-nitro-phenylpropiolic acid, depends upon similar rearrangements.

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[173] Berichte. **9**, 1345. [174] Ibid. **13**, 288. [175] Ibid. **13**, 2259.

LECTURE XV.

THE FUNDAMENTAL CONCEPTIONS OF CHEMISTRY—PHENOMENA OF DISSOCIATION—ABNORMAL VAPOUR DENSITIES—CONSTANT OR VARIABLE VALENCY—THE DOCTRINE OF VALENCY IN ORGANIC CHEMISTRY—THE PERIODIC LAW—LATER DEVELOPMENT OF THE DOCTRINE OF AFFINITY—SPECTRUM ANALYSIS—SYNTHESIS OF MINERALS—CONTINUITY OF MATTER IN THE LIQUID AND GASEOUS STATES—LIQUEFACTION OF THE SO-CALLED PERMANENT GASES—THERMO-CHEMISTRY—ELECTRO-CHEMISTRY—PHOTO-CHEMISTRY—MOLECULAR PHYSICS—MORPHOTROPY.

HAVING now followed organic chemistry in some of its more recent discoveries, and having obtained a knowledge of its remarkable progress under the influence of the theory of valency, it is appropriate to suggest and to discuss the question whether this theory is capable of serving as a fundamental principle in mineral chemistry; and also to recount some of the most important results of investigations in general chemistry.

Before passing on, however, to this part of our task, the theories themselves must be subjected to a more minute consideration and scrutiny. In describing how they have come into existence we have not always been able to enter into the exact significance of their fundamental conceptions. We shall now turn our attention to this matter, although, naturally, it is only possible to bring forward the most important points. For the remainder, the reader is referred to the standard text-books of theoretical and general chemistry.

Our views rest essentially on the precise formulation and distinction of the conceptions of atom, molecule, and equivalent.

An atom is defined as the smallest indivisible quantity of an element which exists under any circumstances; and most generally it only exists in combination with other atoms.

A molecule is defined as the smallest quantity of a chemical substance that occurs in the free state, whether the substance be elementary or compound. The determination of the molecular weight depends essentially upon our combining the conceptions of the physical and of the chemical molecule; that is to say, we apply the word molecule to the smallest quantity of a substance which occurs free in the gaseous state, as well as to the smallest quantity that enters into a reaction.

With respect to determinations of atomic weights, it is to be remarked here that the numbers proposed by Gerhardt[1] were subjected to an important alteration in so far that the atomic weights of all the metals were doubled, except those of the monatomic ones (*i.e.*, the alkali metals and silver). As early as 1840, when the atomic weights of Berzelius were still in use, Regnault had proposed to halve the atomic weight of silver, and, in accordance with this proposal, to assume two atoms of metal in silver oxide for one atom of oxygen.[2] He afterwards made a similar proposal with respect to the atomic weights of potassium, sodium, and lithium.[3] The reason was, that his classical experiments on specific heat had shown him that Dulong and Petit's law only applied to these metals when this assumption was made. Had this proposal of Regnault's been adopted at that time, our present atomic weights would (with few exceptions) have been obtained. But since, following Gerhardt's lead, the atomic weights of all the metals were halved, it was afterwards necessary (when the desirability of Regnault's proposal had been shown upon new grounds, especially by H. Rose[4] and by Cannizzaro[5]) to double them again, with the exception of those of the metals mentioned above. Cannizzaro in particular, showed, in his pamphlet referred to below, that the law of Dulong and Petit was a guide in the determination of the atomic weights, just as the hypothesis of Avogadro was in that of the molecular weights. Even at this time the carrying out of these principles was still confronted by great difficulties. It is true that Deville and Troost[6] showed, at this date, that the vapour density of sulphur, at about 1000°, was only one-third of the number previously found by Dumas and Mitscherlich (compare p. 105) at lower temperatures; so that it was possible to adopt the molecular formula S_2 for sulphur. The anomalies previously observed in the cases of mercury, phosphorus, and arsenic, remained, however; but these were not an obstacle to Cannizzaro. The chemical relations had to stand aside in order to procure acceptance of the principle. He assumed that only one-fourth of a molecule of phosphorus and of arsenic, respectively, was contained in two volumes of phosphuretted and of arseniuretted hydrogen; whilst half a molecule of nitrogen is present in two volumes of ammonia, and a molecule of mercury in two volumes of mercuric chloride. Consequently the divisibility of the molecule is different, according to Cannizzaro, even in chemically analogous substances. Even although this appeared to be a bold view, still no decisive reasons could be established against it.

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[1] Compare, for example, Gerhardt, Introduction à l'Étude de la Chimie, 1848, 29. [2] Ann. Chim. [2] 73, 5; Annalen. 36, 110. [3] Ann. Chim. [3] 26, 261. [4] Pogg. Ann. 100, 270. [5] Nuovo Cimento. 7, 321; also Répert. de Chimie pure. 1, 201; compare Sunto di un Corso di Filosofia Chimica, 1858, 35.

The assumption of differences of constitution amongst the elementary molecules, although striking at first, seemed after a time to be fully justified. Why should not a state of matters be met with in the case of the elements similar to that observed amongst compound substances, the molecules of which are known to present the greatest variety with respect to the numbers of their atoms? Cannizzaro very aptly compares the elements with the hydrocarbons—the molecules of hydrogen, oxygen, etc., with the so-called alcohol radicals, methyl, ethyl, etc., and the molecules of mercury, zinc, and cadmium, with the olefines, a view which may also be extended to the derivatives of both classes of substances:—[7]

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[6] Comptes Rendus. **49**, 239; Annalen. **113**, 42.

[7] Wurtz, Leçons de philosophie chimique. 172.

H_2, O_2, N_2	corresponding to	$(CH_3)_2$, $(C_2H_5)_2$
Hg, Zn	,,	C_2H_4, C_3H_6
K_2O, H_2O	,,	$(CH_3)_2O$, $(C_2H_5)_2O$
CaO, ZnO	,,	C_2H_4O, C_3H_6O
Bi_2O_3, Sb_2O_3	,,	$(C_3H_5)_2O_3$
SnO_2, SiO_2	,,	CO_2
KOH	,,	CH_3OH, C_2H_5OH
$Ca(OH)_2$	,,	$C_2H_4(OH)_2$, $C_3H_6(OH)_2$
$Bi(OH)_3$	,,	$C_3H_5(OH)_3$
$Sn(OH)_4$	,,	$C_4H_6(OH)_4$

Of decisive importance, however, as regards the nature of the molecule of mercury, are the experiments of Kundt and Warburg,[8] which may be adopted as a direct proof of Cannizzaro's view. These physicists, by observing the velocity of sound in mercury vapour, determined the ratio of the specific heats at constant pressure and at constant volume to be 1.67—a number furnished by the mechanical theory of heat, on the assumption that the total energy of the gas consists of the translatory motion of the molecules. The demonstration, furnished by Victor Meyer, of the variable vapour density of iodine,[9] which, as Crafts in particular has shown,[10] eventually sinks to one-half of the original density and then remains constant, can only point to the fact that the molecule of iodine, at high temperatures, consists of a single atom.

A great deal more trouble was experienced in fixing the molecular weights of compounds, in those cases where the numbers calculated from the vapour densities did not agree with those deduced from the chemical relationships of the substances. In his determinations of the relative densities of vapours, Bineau obtained such remarkable numbers that he considered decomposition to be the cause of the peculiar volume relations.[11] Thus he found the density of ammonium carbamate (anhydrous carbonate of ammonia, as he calls it) to correspond to six volumes, whence he assumes a decomposition into four volumes of ammonia and two of carbonic anhydride. Mitscherlich made a similar assumption in the case of antimony pentachloride,[12] and so did Gladstone[13] in that of phosphorus pentabromide. In both of these cases it was assumed that, besides the halogens, the trichloride and the tribromide of the respective elements had been produced. Cahours[14] also expressed the same view in 1847, in explanation of the low vapour density of phosphorus pentachloride.

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[8] Berichte. **8**, 945. Pogg. Ann. **157**, 353.

[9] Berichte. **13**, 394.

[10] Comptes Rendus. **92**, 39.

[11] Ann. Chim. [2] **68**, 434; **70**. 272.

In the same year, Grove[15] made the remarkable observation that water is decomposed into its elements by contact with brightly glowing platinum,—a circumstance which he sought to explain as a result of the high temperature. This view met, however, with little acceptance, the fact that platinum can be melted by means of the oxy-hydrogen flame being looked upon as opposed to it. Consequently, Grove's experiment was regarded as a result of the action of affinity; and it was explained as exactly similar to the decomposition of water (observed by Regnault) by means of melting silver, where silver oxide and hydrogen were supposed to be formed.[16]

Grove's way of regarding the matter was first definitely proved by Henry St. Claire Deville as the result of a very detailed investigation which constitutes the basis of the theory of dissociation.

Before passing on to describe more minutely these phenomena, which are highly important for chemistry, I must here point out that the views with respect to them have been affected by the advances which have meanwhile been made in our knowledge of heat. These advances have been called forth by the law of the conservation of energy, which, as is well known, was first clearly formulated by J. R. Mayer;[17] and they find their expression especially in the mechanical theory of heat and in the kinetic theory of gases, developed chiefly by Clausius, Joule, Rankine, Thomson, Helmholtz, Maxwell, and others.

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[12] Pogg. Ann. **29**, 227.

[13] Phil. Mag. [3] **35**, 345.

[14] Ann. Chim. [3] **20**, 369.

[15] Phil. Trans. 1847, 1; Annalen. **63**, 1.

[16] Ann. Chim. [2] **62**, 367.

[17] Annalen. **42**, 233.

After drawing attention to the fact that the affinity of silver for oxygen could not come into play in Regnault's experiment (since silver oxide breaks up into its constituents at much lower temperatures, and the same thing must certainly take place in presence of hydrogen), Deville shows that the decomposition of water by means of strongly heated lead oxide (at 1200° to 1300°) is also observed. He succeeds in effecting the same decomposition by means of ingeniously contrived apparatus, without the action of a foreign substance; and in this way his opinion that the decomposition is a result of the high temperature is confirmed in an elegant manner.[18]

The difficulty in these investigations arises from the fact that the constituents separated during the decomposition, combine again at lower temperatures, so that the decomposition which has occurred is not recognisable under ordinary circumstances. The proof that decomposition has occurred may be furnished, as Deville shows, (1) by diluting the products of the decomposition by means of a rapid current of an indifferent gas, so that complete recombination is prevented; (2) by diffusion, whereby the composition of the gaseous mixture is altered; or (3) by means of the so-called *tube chaud et froid; i.e.*, by sudden cooling of the products of decomposition.

In the forms of apparatus constructed to carry out these methods, Deville succeeded in proving not only the decomposition of water into hydrogen and oxygen, but also that of carbonic anhydride into carbonic oxide and oxygen, of carbonic oxide into carbon and carbonic anhydride, of hydrochloric acid into chlorine and hydrogen, of sulphurous anhydride into sulphuric anhydride and sulphur, etc.

Supported by these experiments, Deville compares the formation of compounds with the condensation of vapours. According to him, both changes begin at definite temperatures and both proceed gradually. Certain quantities of heat are given out during the condensation of vapours, and the same thing takes place (frequently to a much greater extent) in the combination of two substances. But further, in exactly the same way that evaporation begins below the condensing point, the decomposition of substances can be observed below the true combining temperature. As every degree of the thermometric scale corresponds to a definite vapour pressure, so, in certain cases at least, the pressures of the products of decomposition can be stated. Deville distinguishes between decomposition by the action of heat and decomposition by chemical means. He applies the name dissociation to the former only.[19] It is characterised by the facts that its different phases can be observed ; that it begins at one definite temperature and is completed at another ; and that between these limits the pressures increase from 0 to 760 mm. and more of mercury, so that a definite pressure, due to the gaseous products of the decomposition, corresponds to every temperature.

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[18] Comptes Rendus. **56**, 195, 322, 729; compare also Deville, Leçons sur la dissociation, 1864.

Subsequent experiments on this subject (of a very detailed character) have confirmed Deville's views, in general at least. Only those decompositions are now regarded as examples of dissociation which take place in opposition to the chemical forces and are accompanied by the absorption of heat.[20] The comparison of these phenomena with evaporation, even if it is not quite generally applicable, still holds in the decomposition of solid substances with the formation of gaseous constituents, as was shown by Debray in the case of calcium carbonate,[21] by Naumann in that of ammonium carbonate,[22] by Isambert in that of ammonium hydrosulphide,[23] and by others. Investigations of the compounds of silver chloride with ammonia[24] and of compounds containing water of crystallisation, came to be of special importance, because in the cases of these substances the different compounds with ammonia and the different stages of hydration of the salts, respectively, were indicated by the abrupt variations of the pressure.[25]

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[19] Annalen. **105**, 383. [20] Compare Horstmann, Theoretische Chemie. 666. [21] Comptes Rendus. **64**, 603 ; Bull. Soc. Chim. **7**, 194. [22] Berichte. **4**, 779. [23] Comptes Rendus. **92**, 919 ; **93**, 731. [24] Isambert, Ladenburg's Handwörterbuch der Chemie. **3**, 400 ; Horstmann, Berichte. **9**, 749.

Pfaundler[26] endeavoured to explain the, at first, surprising fact of a partial decomposition which gradually increased with rise of temperature, involving, as it did, the different behaviour of similar molecules under the same conditions. Naumann[27] further developed these views, and they were more definitely formulated by Horstmann,[28] who made use of Maxwell's probability theory[29] of the distribution of the velocities.[30] A close agreement between this theory and the observations was noted in various cases.

Horstmann was the first who tried to establish a general theory of dissociation,[31] starting from the principles of the mechanical theory of heat—especially from the so-called second law. This was found to be in complete accord with the results of experiment in one case.[32] The researches of Gibbs[33] and of Helmholtz,[34] which were based upon similar principles, were more comprehensive and were highly productive.

These investigations, which belong, in part, to the domain of physics, have become of great importance with respect to the question we have here to consider. Shortly after the first researches of Deville, the opinion was stated by three different chemists—Cannizzaro,[35] Kopp,[36] and Kekulé[37]—that the so-called abnormal vapour densities were to be explained as due to the substances concerned breaking up into two or more constituents. The latter were supposed to re-combine on cooling, so that no decomposition was perceptible upon distillation.

The difficulties which thus stood in the way of a direct proof of decomposition, were only overcome some years afterwards by Pebal,[38] who based his experiments on the statement, first made by Bunsen,[39] that it was only possible to distinguish mixtures of gases from homogeneous gases by physical methods (diffusion or absorption). On causing the mixture of gases obtained by heating ammonium chloride to diffuse through an asbestos plug, Pebal was able to show, by the colours imparted to litmus, that the gas in one part of the apparatus possesses an alkaline and in another part an acid reaction.

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[25] Debray, Comptes Rendus. **66,** 194; G. Wiedemann, Pogg. An Jubelband 1874, 474. [26] Pogg. Ann. **131,** 60. [27] Annalen. Supplemen band **5,** 341. [28] Berichte. **1,** 210. [29] Phil. Mag. [4] **19,** 22; **35.** 18 [30] Compare also Boltzmann, Wiedem. Ann. **22,** 31. [31] Annalen. Supp mentband **8,** 112; **170,** 192. [32] Ibid. **187,** 48. [33] Silliman's Journal. 6, 441; **18,** 277. [34] Berlin. Akad. Ber. 1882, 22, 825; 1883, 647. [35] Nuc vo Cimento. **6,** 428; **7,** 375; **8,** 71. Compare also Répert. de Chimie p re. **1,** 201. [36] Annalen. **105**, 390. [37] Ibid. **106,** 142.

In a similar manner, by means of diffusion, Wanklyn and Robinson[40] endeavoured to show the breaking up of sulphuric acid into sulphuric anhydride and water, and of phosphorus pentachloride into phosphorus trichloride and chlorine.

Deville attacked the conclusions which these chemists drew from their experiments.[41] According to him, complete decomposition was not necessary in order to accomplish a separation of the constituents by means of diffusion, a dissociation involving a slight increase of pressure being quite sufficient. As the products of decomposition are carried forward, further quantities are formed, so that, given a sufficiently long duration of the experiment, a complete separation of the constituents is attained at a temperature which only corresponds to a very slight decomposition. Deville points out that the vapour density of water is still normal at 1000°, while at this temperature it can be shown by diffusion that dissociation has already taken place;[42] and hence he considers that the abnormal vapour density must be ascribed to the undecomposed vapour of ammonium chloride. He finds what he regards as a positive proof of this, in the considerable rise of temperature which he believes he can recognise upon the intermixture of ammonia and hydrochloric acid gases in a vessel previously heated to 350°.[43] Wanklyn and Robinson having raised the objection that the gases had not been sufficiently heated prior to their intermixture,[44] Deville afterwards repeats the experiment in a manner which no longer permits of this objection being raised, and again observes a rise of temperature, the amount of which, however, he does not state.[45] He finds a further argument in his favour in the fact that ammonia, when heated to 1100°, breaks up into nitrogen and hydrogen. In his opinion ammonium chloride, after having been heated to this temperature, ought to yield these two gases on cooling as evidence of the formation of ammonia; but this is not the case.

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[38] Annalen. 123, 199. [39] Bunsen, Gasometrische Methoden, 1857, 242. [40] Comptes Rendus. 56, 547. [41] Ibid. 56, 729. [42] Deville, Leçons sur la dissociation, 365. [43] Comptes Rendus. 56, 729.

In opposition to this argument, Than adduces the fact that a gaseous mixture is much more difficult to decompose than a pure gas,[46] and this is in complete agreement with Deville's views regarding dissociation.[47] By diminishing the partial pressure, the temperature at which dissociation begins is raised;[48] or, the temperature remaining the same, the pressure due to decomposition is diminished. Further, Than observed no rise in temperature on mixing hydrochloric acid and ammonia at 360°. Even if the errors were greater in his arrangement of the experiment, and assuming that he was unable to measure very small differences of temperature, still it is placed beyond doubt by his statements that only inconsiderable quantities of heat are liberated by the intermixture of ammonia and hydrochloric acid at 360°. This is confirmed by an experiment by Marignac,[49] who was able to show that just as much heat is evolved in the formation of ammonium chloride from ammonia and hydrochloric acid as is required for its volatilisation. Hence it may be looked upon as fully proved that ammonium chloride does not exist in the gaseous state, but that it breaks up, on volatilisation, into its components.

Similar facts, even if not always so convincing, have also been observed in the cases of many other compounds whose molecules in the gaseous state correspond to four volumes; as, for example, phosphorus pentachloride,[50] ammonium sulphide,[51] ammonium carbamate,[52] etc. A lengthy discussion took place between Wurtz on the one hand,[53] and Troost,[54] Deville,[55] and Berthelot[56] on the other, regarding the nature of the vapour obtained from chloral hydrate. This discussion ended in favour of the former, and led to the proof of the decomposition of chloral hydrate upon vaporisation.

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[44] Comptes Rendus. **56**, 1237. [45] Ibid. **59**, 1057. [46] Annalen. **131**, 129. [47] Deville, Leçons. 364. [48] Compare Naumann, Annalen. Supplementband **5**, 341. [49] Comptes Rendus. **67**, 877.

Returning now to the definitions of our fundamental conceptions (compare p. 297), we designate as the equivalent, or better, the equivalent weight, that quantity of an element or of a radical which can replace or combine with one atom of hydrogen. This conception, however, no longer plays any essential part; another one, which stands in close relationship to it, having been introduced instead of it,—that, namely, of valency or atomicity. By this term we understand the quotient obtained by dividing the atomic weight by the equivalent, and it was discussed at length in the preceding lecture. The question as to whether the valency of any given element is constant or variable is one of particular importance. So long as we are satisfied to formulate and to make use of our conception of valency in harmony with the above definition, constant valency may, of course, be assumed. As soon, however, as we compare (as it is necessary that we should do) the valencies of the multivalent elements with one another, we can no longer assert the absolute constancy of the valency of any element. Even in the case of carbon, where the assumption of a uniform quadrivalence encounters relatively few exceptions, the existence of carbonic oxide is at variance with its universal accuracy. We find a similar thing, only to a greater extent, in the cases of the other elements, and are therefore obliged to admit the possibility of exceptions in every case.

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[50] Cahours, Ann. Chim. [3] **20**, 369; Deville, Comptes Rendus. **62**, 1157.

[51] Horstmann, Annalen. Supplementband **6**, 74.

[52] Naumann, ibid. **160**, 1.

[53] Comptes Rendus. **84**, 977, 1183, 1262, 1347; **85**, 49; **86**, 1170; **89**, 190, 337, 429, 1062; **90**, 24, 118, 337, 572.

[54] Ibid. **84**, 708; **85**, 32, 144, 400; **86**, 331, 1394.

[55] Ibid. **84**, 711, 1108, 1256.

[56] Ibid. **84**, 1189, 1269; **85**, 8; **90**, 112, 491.

Two different methods have been proposed in order to bring these exceptions as far as possible into harmony with the system, but neither of them wholly gets rid of the difficulty.

One party, under the leadership of Kekulé,[57] adheres to the definition of valency given above, but admits that there is a large class of substances to which it is not applicable. This class is composed of the molecular compounds, the smallest particles of which consist of aggregates of molecules held together by means of molecular forces. Examples of the class are the compounds containing water of crystallisation (also alcohol, benzene, etc., of crystallisation), the majority of double salts, the ammonium salts, phosphorus pentachloride, iodine trichloride, etc. No precise definition of them can be given, but they are characterised generally by the facts that they cannot pass, undecomposed, into the state of vapour (although Thorpe found phosphorus pentafluoride to be an exception to this rule[58]), and that they are easily formed from and decomposed into their molecular constituents.

The adherents of constant valency are further obliged to recognise the unsaturated compounds as exceptions. Even although there are not a very great many of these compounds, still their existence constitutes a serious objection to the doctrine; and fruitless endeavours have been made to weaken this objection on the ground of the tendency exhibited by such substances to become saturated.[59]

The opponents of these views, whose first representatives are Frankland and Couper,[60] define the valency of an element as its maximum saturating capacity, and under this definition the unsaturated compounds cease to occupy an exceptional position. In view of the fact that they further assume the valency in the case of many elements to be considerably higher than had previously been assumed—nitrogen and phosphorus, for example, as quinquivalent, sulphur as sexivalent, iodine as quinquivalent or septivalent—it is possible for them to include in the system a large number of molecular compounds. But it also becomes necessary for the adherents of this view to explain the change in the saturating capacity, or at least to establish the conditions which bring about this change in the properties of the elements, if their hypotheses are to deserve the name of a theory. Very little has yet been done in this direction, however, and the little that has been done is scarcely capable of any general formulation.[61] On the other hand, a number of facts have become known which can only be explained with difficulty on the assumption of constant valency; such, for example, as the identity of the naphthyl-phenyl sulphones and of the tolyl-phenyl sulphones which can be prepared in different ways;[62] or such as the isomerism of the two triphenyl-phosphine oxides, one of which, $P(C_6H_5)_3O$, is supposed to correspond to phosphorus pentachloride; and the other, $P(C_6H_5)_2OC_6H_5$, to phosphorus oxychloride.[63]

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[57] Lehrbuch der Chemie. 1, 142, 443; Comptes Rendus. **58**, 510.
[58] Annalen. **182**, 204.
[59] Compare p. 269 and Horstmann, Theoretische Chemie. 295.
[60] Compare pp. 231 and 254.

It is clear from these few observations that the subject of valency, quite apart from any mathematical basis (whch is at present altogether wanting[64]), must still be called a very anomalous and uncertain one, and that there is no existing conception of it which is capable of dealing in a logical manner with the whole domain of chemistry.

That the idea is still retained, in spite of this, and that it is even yet regarded as one of the most important principles, is explicable, in organic chemistry at least, on account of the almost marvellous consequences which the latter branch of the subject is able to show as the result of its assistance during the last fifty years. In inorganic chemistry, however, the state of matters is very different.

No doubt a favourable and helpful influence may be observed in inorganic chemistry also; and, in particular, classification has become essentially clearer, as I wish to illustrate in individual cases. The possibility of classifying the elements themselves according to their valencies indicates a step in advance, since analogies were thereby brought out which had only been partially recognised previously. The analogy of carbon with silicon had already been pointed out, but boron had also been placed along with these two. The analogy of the two former was now established much more clearly, whilst boron was recognised as belonging to another series altogether. On the other hand, titanium, zirconium, and tin were classed along with carbon and silicon. Similarly arsenic, antimony, and bismuth took their places beside nitrogen and phosphorus, then vanadium also, as a consequence of Roscoe's careful investigation,[65] and, finally, niobium and tantalum when the results of Marignac's researches were published.[66] A similar thing took place with the metals, which had hitherto been arranged either according to their relative densities or to their analytical behaviour. The theory of valency exercised, further, a decided influence upon the views respecting many classes of compounds. This was the case with the silicates in particular. Wurtz showed how the facts ascertained by him with respect to the condensations of glycol might be extended to the derivatives of silicic acid,[67] and, by so doing, he brought sudden light into a hitherto obscure region. Soon afterwards this region was further illuminated by Tschermak's[68] important research on the felspars, in accordance with which these substances must be regarded as isomorphous mixtures of orthoclase, albite, and anorthite. The numerous metal-ammonia and metal-ammonium compounds now found a place in the system also, being looked upon as ammonia or as ammonium chloride with hydrogen atoms replaced by metal or metallic oxide. Hofmann was the first to attempt this classification,[69] and in doing so, he turned to account the results of his researches on organic bases. The same idea was more fully carried out by Weltzien,[70] H. Schiff,[71] Cleve,[72] and many others.

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[61] Compare, however, Horstmann, Theoretische Chemie. 327 *et seq.*; Van 't Hoff, Ansichten über die Organische Chemie. **1**, 3.

[62] Michael and Adair, Berichte. **10**, 583; **11**, 116.

[63] Michaelis and Lacoste, ibid. **18**, 2118.

[64] Compare, however, Kekulé, Annalen, **162**, 86; Baeyer, Berichte. **18**, 2277.

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[65] Annalen. Supplementband **6**, 77.

[66] Ann. Chim. [4] **8**, 5 and 49 (abstract); Annalen. **135**, 49; Ann. Chim. [4] **9**, 249; Annalen. Supplementband **4**, 350.

[67] Répert. de Chimie pure. **2**, 449; Leçons de philosophie chimique, 181.

[68] Pogg. Ann. **125**, 139.

[69] Annalen. **78**, 253; **79**, 11.

Despite all this, it cannot be said that the theory of valency has proved very productive in inorganic chemistry. In the first place, the number of researches which it has occasioned is by no means very considerable; and, further, a systematic treatment of the subject, based upon valency, is not capable of being uniformly and logically carried out. Another hypothesis has had a far more important and lasting effect, and is now able to show the most brilliant and undreamt-of results. I must here discuss the relations which have been found to subsist between the atomic weights and the properties of the elements.

The more recent investigations on this subject are related to Prout's hypothesis, which has already been considered.[73] It is true that this hypothesis never became generally accepted, but nevertheless it occasioned speculations from time to time in the same direction. I only mention here Döbereiner, who, in 1829, first drew attention to what he called the triads,[74] (that is, to groups of three analogous elements possessing atomic weights such that one of them might be regarded as the arithmetical mean of the other two). Gmelin,[75] Pettenkofer,[76] Dumas,[77] and Lenssen[78] further elaborated these ideas, without arriving at any results specially worth mentioning.

A valuable result was, however, attained by the proof that the properties of the elements are periodic functions of their atomic weights. For this, we are indebted to the investigations of Newlands,[79] Lothar Meyer,[80] and Mendelejeff.[81] The chief merit unquestionably belongs to the latter, who first gave prominence to the existing relations in a quite general form, and (what must be regarded as specially important) pointed out clearly the advantages of considerations of the kind. It is for this reason that his paper at once made a great sensation, whereas that of Newlands remained quite unnoticed.[82]

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[70] Annalen. **97**, 19.
[71] Ibid. **123**, 1.
[72] Bull. Soc. Chim. [2] **7**, 12; **15**, 161; **16**, 203; **17**, 100, 294.
[73] Compare p. 102.
[74] Pogg. Ann. **15**, 301.
[75] Handbuch. Third Edition, **1**, 35.
[76] Annalen. **105**, 187.
[77] See p. 102.
[78] Annalen. **103**, 121; **104**, 177.
[79] Chem. News. **10**, 59, 94; **13**, 113.
[80] Moderne Theorien. First Edition, 136; Annalen. Supplementband **7**, 354.
[81] Zeitschrift für Chemie. **12**, 405; Annalen, Supplementband **8**, 133.

In the tabulation adopted by Mendelejeff, the elements are arranged according to their atomic weights ; but they are further arranged into divisions in such a way that the elements which are analogous to one another fall into vertical columns and form groups, whilst each set of from seven to ten elements succeeding one another in a horizontal line in the order of their atomic weights, constitutes a short period within which the properties (physical as well as chemical) progressively vary. Two successive horizontal series form a long period in connection with which it is to be noted that, in the groups, the analogies between elements of the even, and also of the uneven, horizontal series, are greater amongst themselves than those between elements which belong partly to the even and partly to the uneven series.

Of the applications of the "periodic law," the two following have attained special importance :—(1) The determination or correction of the atomic weights of insufficiently investigated elements, and (2) the prediction of the properties of unknown elements.

With respect to the first of these applications the following facts must be mentioned here. In conformity with the proposal of Awdejeff,[83] Mendelejeff assumed the atomic weight of beryllium to be 9, and placed this element in a group along with magnesium ; whereas it had hitherto been regarded by many chemists as a metal akin to aluminium, and of atomic weight 13.5. This new view called forth a prolonged discussion, which terminated, however, with the complete triumph of Mendelejeff's opinion.[84]

The atomic weight of indium was assumed to be 113, or one and a half times as great as previously, and this number was very soon confirmed by the determination of the specific heat of the metal by Bunsen[85] and by Mendelejeff.[86] The atomic weight of uranium was doubled—a proceeding which was found by the excellent and detailed investigations of Zimmermann[87] to be in complete agreement with the facts. Finally, it may be pointed out that Mendelejeff adopted 125 as the atomic weight of tellurium, in opposition to the previous determinations which had furnished the number 128. This was also apparently confirmed by the redetermination of the atomic weight in a specially purified sample,[88] but Brauner's most recent experiments gave essentially different results.

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[82] With respect to the question of priority, compare Newlands, Chem. News. 32, 21, 192 ; L. Meyer, Berichte. 13, 259 ; Mendelejeff, ibid. 13, 1796. [83] Pogg. Ann. 56, 101 ; compare also Klatzo, J. pr. Chem. 106, 227. [84] Nilson and Pettersson, Berichte. 11, 381 ; 13, 1451 ; 17, 987 ; L. Meyer, ibid. 13, 1780 ; Reynolds, ibid. 13, 2412 ; Nilson, ibid. 13, 2035.

But Mendelejeff's predictions respecting new elements have been followed by results which are simply marvellous. In order to render possible the arrangement into groups and series, and to attain approximately equal differences in successive members, blanks had to be left, which, according to Mendelejeff, would be filled up by existing, but at that time unknown, elements. He was able to foretell the atomic weights and other properties of these elements from their position in the system, with the aid of the properties observed in the groups and series, which, like a system of co-ordinates, could be called in to assist. Three such blanks occurred in the first five series, and these he indicated as representing the positions of eka-boron (at. wt. 44), eka-aluminium (at. wt. 68), and eka-silicon (at. wt. 72). Since that time, these three elements have been discovered, and they have been found to possess, approximately, the properties predicted by Mendelejeff. They are: scandium, discovered by Nilson,[89] with atomic weight 44.1; gallium, discovered by Lecoq de Boisbaudran,[90] with atomic weight 70; and germanium, discovered by Winkler,[91] with atomic weight 72.

But these are not the only results which render this theory most valuable. The theory has so thoroughly permeated the whole of chemistry, that investigations of the elements and of their compounds have gained a new significance. As a result of the bond which it establishes between the individual elements, it lends to every such special investigation the charm of a research of universal interest.

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[85] Pogg. Ann. **141**, 1. [86] Bull. de l'Acad. Imp. de St. Petersbourg. **16**, 45. [87] Annalen. **213**, 285; **216**, 1. [88] Brauner, Berichte. **16**, 3055; compare p. 349. [89] Berichte. **12**, 550, 554; **13**, 1439. [90] Comptes Rendus. **81**, 493, 1100; **86**, 475, etc. [91] J. pr. Chem. [2] **34**, 177.

Investigations which deal with the subject of affinity, presenting this subject in a mathematical form and combining it with Berthollet's doctrine of affinity, are of equal importance.

We possess investigations of this kind, in a finished state, which have been tested in the most different directions and have been found accurate; so that in this respect also great results have been attained. An investigation by Guldberg and Waage [92] constitutes a new departure for advancement in this direction. In place of Berthollet's notion of chemical mass, these investigators introduced that of active mass, by which they understand the quantity of a substance contained in a unit of space. The chemical energy with which two substances act upon one another is then equal to the product of their active masses multiplied by the affinity coefficients; and by the latter Guldberg and Waage understand values which are dependent upon the chemical nature of the substances and upon the temperature.[93]

When the substances A and B are transformed, in a chemical operation, into A' and B', and where, conversely, A' and B' can be transformed into A and B, equilibrium is established when the forces acting between A and B are equal to those acting between A' and B'. If the active masses A and B are represented by p and q, and those of A' and B' by p' and q', and further, if the affinity coefficients are k and k', then in order that equilibrium may be established we must have—

$$k\,p\,q = k'\,p'\,q'$$

In applying this equation it is advisable to introduce, instead of the quantities p, q, p', and q', the relative numbers of molecules; that is, the quotients obtained by dividing the quantities present by the molecular weights.

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[92] Etudes sur les affinités chimiques. Christiania 1867; J. pr. Chem. [2] **19**, 69.

[93] Compare also Van't Hoff, Berichte, **10**, 669.

This "law of chemical mass action" has been tested in various ways, and the observed facts have repeatedly been found in agreement with it. In this connection, mention must first be made here of investigations which were carried out by Wilhelmy, by Berthelot and Péan de Saint Gilles, and by Vernon Harcourt and Esson, all of whom must be regarded as precursors of Guldberg and Waage.[94] Wilhelmy introduced the idea of velocity of reaction as early as 1850, and thus more than fifteen years prior to the investigations of Guldberg and Waage. In a highly interesting research on the inversion of cane sugar,[95] he showed that the quantity of sugar inverted in unit time is proportional to the total quantity of sugar present. Berthelot and Péan de Saint Gilles[96] studied the limit of ester formation and the velocity of the reaction, and the numerical values found are sufficiently close to those calculated from theory. These experiments were continued and extended by Menschutkin,[97] who examined the ester formation in the direction referred to, in the cases of the most different alcohols and acids, and thus furnished an important contribution to the varying behaviour of substances of different structure. Vernon Harcourt and Esson arrived at results which are in conformity with the general law, in their investigation of the reduction of potassium permanganate by oxalic acid added in great excess,[98] and in their later work on the action of hydrogen peroxide on hydriodic acid.[99] Bearing also upon this subject are the detailed thermo-chemical researches of Thomsen,[100] and the studies of Ostwald[101] on chemical volume, which not merely confirmed the theory but also extended it. These investigations are chiefly connected with the affinity relations between acids and bases. The conception of avidity is here introduced —an idea approximately corresponding to what used to be somewhat less precisely designated as the strength of acids or of bases. What is understood by this term is the proportion in which two substances are shared by a third, the quantity of which is insufficient for their complete saturation ; and it appears that the avidity is proportional to the square root of the affinity coefficient.

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[94] According to Ostwald (Allgemeine Chemie, 2nd Ed. II. part 2, 40), Wenzel had already stated the most important proposition of the doctrine of affinity, that the intensity of the chemical action is proportional to the concentration of the acting substance.

[95] Pogg. Ann. **81**, 413 and 499.

[96] Ann. Chim. [3] **65**, 385; **66**, 5; **68**, 225.

[97] Berichte. **10**, 1728, 1898; **11**, 1507, 2117, 2148; **13**, 162, 1812; **14**, 2630. Annalen. **195**, 334; **197**, 193. Ann. Chim. [5] **20**, 289; **23**, 14; **30**, 81.

[98] Phil. Trans. 1866, 193.

[99] Ibid. 1867, 117.

[100] Pogg. Ann. **138**, 65; and Thermochemische Untersuchungen. **1**.

[101] J. pr. Chem. [2] **16**, 385; **18**, 328; **19**, 468; **25**, 1; Pogg. Ann. Ergänzungsband **8**, 154; Wiedem. Ann. **2**, 429, 671.

Other important investigations are those of Horstmann[102] on the incomplete combustion of carbonic oxide and of hydrogen ; that on the partial decomposition of ferrous salts by water, which G. Wiedemann[103] carried out by the aid of a magnetic method ; and that on the ratio of the distribution of acids between two alkaloids, which Jelett[104] ascertained by determining the optical rotatory power. But it is not possible to enter more particularly here into these and many similar researches.[105]

To a certain extent in contrast with these investigations, which are chiefly theoretical, there is the discovery of a method of investigation which may certainly be regarded as one of the most brilliant that has been brought forward in recent times as the result of experimental research. I refer to the method of spectrum analysis, which has enabled us to draw conclusions regarding the chemical composition of distant heavenly bodies whose material constitution was previously altogether unknown, and by the aid of which the number of the known elements has been very considerably increased.

It would take too much space to deal with the early researches prior to the classical investigations of Kirchhoff and Bunsen ;[106] and therefore I refer, with respect to these, to the historical treatment of the subject by Mousson,[107] to some notices by Tyndall,[108] and especially to a paper by Kirchhoff,[109] which deals with them. I must content myself by simply making a few remarks on the matter here.

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[102] Annalen. **190**, 228. [103] Wiedem. Ann. **5**, 45. [104] Trans. Roy. Irish Acad. **25**, 371. [105] Compare the article "Affinität" by E. Wiedemann, in Ladenburg's Handwörterbuch der Chemie, **1**, 114. [106] Pogg. Ann. **110**, 161; **113**, 337 ; compare also Kirchhoff, Berlin. Akad. Abhandl. 1861, 63 ; Untersuchungen über das Sonnenspectrum und die Spectren der chemischen Elemente.

Wollaston, in 1802, first observed the dark lines in the spectrum of the sun.[110] These were more fully examined and determined in 1814 by Fraunhofer,[111] to whom Wollaston's observations were unknown. In 1822, Sir J. Herschel observed the bright bands[112] which the light of a flame coloured by metallic salts exhibits when decomposed. This phenomenon was followed up further by Talbot[113] and by Brewster.[114] Swan pointed out the great delicacy of this reaction, especially in the case of common salt.[115]

Fraunhofer drew attention to the coincidence of the D line with the yellow sodium line. Brewster found the potassium lines to correspond to others of the Fraunhofer lines, and Foucault[116] also made similar observations.

There are two points in particular which are of fundamental importance with respect to spectrum analysis, and these we owe to the researches of Kirchhoff and Bunsen. The first of them is the fact that every element, in the state of incandescent vapour, is characterised by giving a definite discontinuous spectrum, a fact which even Swan did not venture to state with certainty; and the second is the law of selective absorption, which Ångström[117] and Balfour Stewart approached very closely, without actually grasping it fully and clearly.[118] This law is now known as Kirchhoff's law, as it was proved mathematically by Kirchhoff,[119] and experimentally by Kirchhoff and Bunsen by means of the celebrated experiment of the reversal of the lines. The law states that the ratio between the emissive power and the absorptive power is the same for all substances at the same temperature, for rays of the same wave-length. From this it follows that all opaque substances begin to glow at the same temperature—that is, that they give out light of the same wave-length—and that incandescent substances only absorb such rays as they themselves emit. Since, however, incandescent gases possess maxima and minima of light intensity, while solid and liquid substances emit light of every kind when sufficiently heated, the former must also possess a selective absorptive power, and this is not the case in general with the latter.[120] The Fraunhofer lines are thus explained as consequent upon absorptions by means of incandescent vapours. Their existence led to the elucidation of the physical nature of the sun, while the determination of their positions (wave-lengths) and the comparison of them with the emission spectra of the elements in the gaseous state, led to the fixing of its chemical composition. Kirchhoff thus became the founder of a new branch of chemical science—that of stellar chemistry. Although this branch is still comparatively recent, it is already in a position to show great results. By means of it astronomy has met with new problems, and has been furnished with new methods, which have immensely widened its sphere of activity; but it is not possible to enter into this subject more fully here.

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[107] Connaissances sur le spectre ; Bibl. Univers. de Genève [2] **10**, 221.
[108] Phil. Mag. [4] **22**, 155.
[109] Pogg. Ann. **118**, 94.
[110] Phil. Trans. **1802**, 378.
[111] Gilb. Ann. **56**, 278.
[112] Treatise on Light.
[113] Brewster, Edinburgh Journal of Science. **5**, 77 ; Phil. Mag. [3] **3**, 35 ; **4**, 114 ; **9**, 3.
[114] Phil. Mag. [3] **8**, 384 ; Pogg. Ann. **38**, 61 ; compare Comptes Rendus. **62**, 17.
[115] Trans. Roy. Soc. Edin. **21**, 411.
[116] Ann. Chim. [3] **58**, 476.
[117] Pogg. Ann. **94**, 141.
[118] Trans. Roy. Soc. Edin. **22**, 1, 59.
[119] Pogg. Ann. **109**, 275.

The discoverers of the spectroscopic method of analysis were themselves able to establish its importance in chemistry not only by showing its application to analytical chemistry, but also by the discovery of two new elements—caesium and rubidium. We are indebted to the same method for the discovery of thallium by Crookes,[121] and of indium by Reich and Richter;[122] as well as for that of gallium and scandium, of which mention has already been made.[123]

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[120] An exception is furnished by the salts of didymium, which possess a selective absorptive power. [121] Phil. Mag. [4] **21**, 301; Annalen. **124**, 203. [122] J. pr. Chem. **89**, 441. [123] Compare p. 313.

Amongst the more recent investigations in this department some which deserve to be specially mentioned are those of A. Mitscherlich, who was able to show that not merely every element, but every compound possesses, in the gaseous state, a spectrum peculiar to itself,[124] and those of Plücker and Hittorf, who showed that there are two spectra corresponding to every element; *i.e.*, that besides the line-spectrum there is also the band-spectrum.[125] Further, there are the investigations on quantitative spectrum analysis, especially those of Vierordt[126] and of Glan.[127] Finally, there are the numerous researches which are directed towards establishing relations between the emission spectra of the elements, such as those of Lecoq de Boisbaudran[128] and of Ciamician;[129] or between the absorption spectra of compounds, such as those of Abney and Festing,[130] of Krüss,[131] and others.

Forming a counterpart to this analytical method there is also a synthetical one, to which, however, the same general applicability that the former possesses cannot be attributed. I refer to the synthesis of minerals. A stimulus to making experiments of this kind was supplied by observations made by Koch (1809),[132] and especially by Hausmann and Mitscherlich, who found, amongst the slags obtained in metallurgical processes, products which proved to be identical with known minerals. The first successful experiment of this kind originated with Sir James Hall, who prepared crystallised carbonate of lime (marble) by heating the carbonate under pressure.[133] Berthier and Mitscherlich obtained artifical mica, pyroxene, and similar minerals by fusing silica with lime, magnesia, and ferric oxide.[134] Gaudin prepared small rubies by fusing alumina (obtained by heating ammonia alum) in the oxyhydrogen blow-pipe, after the addition of some chromic oxide.[135] Gay-Lussac obtained crystallised hæmatite by the action of water vapour on ferric chloride.[136] Ebelmen succeeded in preparing an extensive series of difficultly fusible or infusible crystalline minerals by employing borax or boracic acid as a material from which to crystallise them.[137] Becquerel obtained, in the crystalline state, substances insoluble in water, such as silver chloride, silver sulphide, cuprous oxide, basic cupric carbonate, etc, by making use of slowly progressing chemical reactions.[138]

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[124] Pogg. Ann. **116**, 499; **121**, 459. [125] Phil. Trans. 1865, 1. [126] Anwendung des Spectralapparates zur Photometrie der Absorptions-spectren. Tübingen 1873. [127] Wiedem. Ann. **1**, 351; compare also Hüfner, J. pr. Chem. [2] **16**, 290. [128] Comptes Rendus. **69**, 445, 606, 657, etc. [129] Ber. Wien. Akad. **76** (2), 499; **79** (2), 8; **82** (2), 425. [130] Journ. Chem. Soc **42**, 130-131. [131] Berichte. **16**, 2051; **18**, 1426. [132] Ueber krystall. Hüttenproducte. [133] Trans. Roy. Soc. Edin. **6**, 71; compare Gehlen's Journal für die Chemie, etc. **1**, 271. [134] Ann. Chim. [2] **24**, 355.

Although I cannot enter into further details here, I may add that Senarmont attacked and, partially at least, solved the problem of determining, and of realising, the conditions under which those naturally occurring minerals are formed which are met with crystallised in veins. In particular, he employed water for this purpose, and he caused it to act under pressure at about 350°.[139] It may further be stated that Sainte Claire Deville[140] and his pupils discovered and made use of the favourable effect of hydrofluoric acid and of other fluorine compounds in promoting crystallisation; and that Hautefeuille[141] was the first who artificially prepared potash and soda felspars. Mention must also be made here of the numerous syntheses of minerals that were carried out by Friedel and his pupils.

The introduction of the idea of the critical temperature or of the absolute boiling-point signalised a great advance in our knowledge of the connection between the different states of aggregation of substances.

Cagniard de la Tour[142] observed, as long ago as 1822, that on heating liquids in sealed tubes which they almost fill, a temperature can be attained at which the meniscus disappears, and the whole presents a perfectly homogeneous appearance. From this he concluded that at this temperature the liquid is converted into gas notwithstanding the pressure. Although these experiments were highly noteworthy, still they did not attract any considerable attention; and it was only thirty-three years later that Wolf[143] and Drion[144] tried to determine, in the cases of a few liquids, the temperatures at which they pass into the state observed by Cagniard de la Tour. Mendelejeff, in 1861, introduced the very appropriate name "absolute boiling-point" to designate this temperature; and he defined it as the temperature at which both the cohesion of the liquid and its heat of evaporation vanish, and the liquid itself is converted into vapour irrespective of pressure and of volume.[145]

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[135] Annalen. **23**, 234. [136] Ann. Chim. **80**, 163; [2] **1**, 33. [137] Comptes Rendus. **25**, 661; Ann. Chim. [3] **22**, 211. [138] Ann. Chim. [2] **51**, 101. [139] Annalen. **80**, 212. [140] Caron and Deville, ibid. **108**, 55; **109**, 242, etc. [141] Comptes Rendus. **90**, 830. [142] Ann. Chim. [2] **21**, 127, 178; **22**, 410.

Eight years later, the celebrated paper of Andrews[146] appeared, in which the connection between pressure, volume, and temperature was accurately examined in the case of carbonic anhydride, which, it was shown, could not be liquefied at temperatures above 30.92° C. Andrews called this the critical temperature; and, further, he designated as critical pressure the pressure which is just sufficient to bring about liquefaction at a temperature infinitesimally below the critical temperature. Andrew's observations enabled him to draw isotherms for carbonic anhydride at different temperatures, which exhibited the relations between pressure and volume. When this had been done, it appeared that the curves were discontinuous below 30.92°, and consisted of different parts. Although slight changes of curvature are observed in the isotherms for temperatures just immediately above 30.92°, these are no longer observed at 48°, the curve at that temperature approximately corresponding, throughout its entire length, to the equation which holds for gases—

$$pv = C,$$

that is, it approximates to a rectangular hyperbola.

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[143] Ann. Chim. [3] **49**, 265. [144] Ibid. [3] **56**, 33. [145] Annalen. **119**, 1.
[146] Phil. Trans. 1869, 575.

As a result of this investigation the definitions of vapour and of permanent gas which had previously been adopted were abandoned, and the word gas is now applied to every substance in the gaseous state when heated above its critical temperature.[147] The continuity of the liquid and gaseous states is observable when a liquid is heated under a pressure greater than the critical pressure. In such a case a separation into liquid and gas never takes place, but the liquid is transformed into gas without the change giving rise to any noticeable heterogeneity.[148]

These investigations exercised a decided influence upon the experiments on the condensation of gases. Faraday, as is well known, was the first to turn his attention to this matter with any considerable result; and quite a number of gases were liquefied by him in an extremely simple and ingenious manner.[149] He operated upon the small scale only, whilst carbonic anhydride was first liquefied in considerable quantities by Thilorier.[150] Faraday then continued his investigations,[151] making use of the knowledge already gained by Thilorier, but without obtaining any result in the cases of hydrogen, oxygen, nitrogen, carbonic oxide, nitric oxide, etc. Natterer was likewise unable to liquefy hydrogen although he exposed it to a pressure of 2790 atmospheres.[152]

It was only in 1877 that Pictet[153] and Cailletet[154] succeeded, nearly simultaneously, in liquefying the majority of the so-called permanent gases; but it was not possible at that time, by the aid of the methods and appliances employed by these investigators, to obtain the liquids in quantity and to determine their physical constants (boiling-point, critical temperature, density, etc.). This was first accomplished by Wroblewsky,[155] whose research may be regarded as an example of finished skill.

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[147] Wroblewsky (Monatshefte. 7, 383) afterwards attacked the conception of critical temperature; but the matter cannot be further discussed here.

[148] Compare Ostwald, Allgemeine Chemie 1, 267.

[149] Phil. Trans. 1823, 160, 189; Alembic Club Reprints, 12, 5, 10.

[150] Ann. Chim. [2] 60, 427.

[151] Phil. Trans. 1845, 155; A.C.R. 12, 33.

[152] Pogg. Ann. 94, 436.

[153] Comptes Rendus. 85, 1214, 1220; Ann. Chim. [5] 13, 145.

[154] Comptes Rendus. 85, 851, 1016, 1213; Ann. Chim. [5] 15, 132.

The intimate connection between physics and chemistry, which is apparent in the matter just dealt with, makes itself still more clearly manifest when we pass on to thermo-chemistry. This is a subject which is of equal importance to both branches, and, moreover, it has been almost entirely elaborated by men belonging to the two sciences. Lavoisier and Laplace may be looked upon as the founders of thermo-chemistry, not only on account of their experimental researches on specific and latent heats and on heats of combustion, but also on account of their masterly definitions,[156] and, especially, of the fundamental (if not quite precisely formulated) principle which they deduce from the mechanical law of the conversation of energy:—

The heat liberated during combination or change of state is consumed again during decomposition or return to the original state, and *vice versa*.[157]

This principle was enunciated by Hess, in 1840, in another form which is very important and strictly accurate for practical thermo-chemistry:—The evolution of heat corresponding to any chemical process is the same whether the process is accomplished in different stages or all at once.[158]

Hess established this principle empirically, and he employed it extensively in order to determine quantities of heat which were incapable of direct measurement—proceeding, therefore, in exactly the same manner as is done at the present day.

The comprehensive researches of Favre and Silbermann[159] are of great value. These consist, in part, of very exact thermal determinations, especially of heats of combustion, and, up till about forty years ago, they constituted the empirical basis of thermo-chemistry. They have now been superseded, however, by the excellent experiments of J. Thomsen and of Berthelot, which embrace almost the whole domain of chemistry.

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[155] Monatshefte. **6**, 204. [156] Compare p. 26. [157] Lavoisier, Oeuvres. **2**, 287. [158] Pogg. Ann. **50**, 385; **52**, 97. [159] Ann. Chim. [3] **34**, 357; **36**, 1; **37**, 406.

Thomsen[160] recognises that the principle of Hess is a deduction from the first law of the dynamical theory of heat, which he adopts as the basis of his theoretical considerations. He then advances a second principle, according to which every simple or complex action, of a purely chemical nature, is accompanied by the evolution of heat; and this he endeavours to establish both theoretically and empirically. The principle in many cases agrees with the results of experiment, but still exceptions are known. These, however, can perhaps be otherwise explained. It may therefore be asserted that chemical forces, when acting independently, always tend to bring about exothermic reactions; whilst endothermic reactions are regarded as consequent upon the action of heat.[161]

Thomsen has endeavoured, more recently, to determine from the numbers found empirically the values of the affinities of carbon, expressed in calories; and from these values, to further deduce the heats of formation of many organic compounds. Here likewise a remarkable agreement has been observed, but exceptions have to be noted in respect to this matter also. It has already been pointed out at the proper place[162] that considerations of this kind can be employed in confirming the structure of organic compounds.

Berthelot[163] advanced three principles, the first of which states that the evolution of heat in chemical processes is a measure of the chemical and physical work done during the actions. The principle is thus an application of the first law of the dynamical theory of heat. According to the second principle, the evolution of heat in a chemical process in which no external work is done, depends only upon the initial and the final states of the system. This is a more precise statement of the principle of Lavoisier and Laplace (compare p. 323). The third principle states that every chemical transformation which is completed without the aid of any external energy, tends to produce that substance or system of substances in whose formation the maximum evolution of heat takes place.

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[160] Pogg. Ann. **88**, 349; **90**, 261; **91**, 83; **92**, 34; **138**, 65. See also Berichte. **2**, 482, 701; **3**, 187, 496, 716, 927; **4**, 308, 586, 591, 597, 941; **5**, 170, 181, 508, 614, 1014; **6**, 233, 423, 697, 710, 1330, 1434; **7**, 31, 379 452, 996, 1002; **9**, 162, 268, 307; **10**, 1017, etc.; Thermochemische Untersuchungen, Four Vols. Leipzig, 1882-86.

[161] Compare Hortsmann, Theoretische Chemie. 612 *et seq.*

[162] Compare p. 278.

[163] Ann. Chim. [4] **6**, 290; **18**, 103; **29**, 94; [5] **4**, 5, etc.; Mécanique Chimique fondée sur la Thermochimie, Two Vols. Paris, 1879.

This "principle of maximum work" raised a great deal of commotion. Not only was its originality contested, since it was looked upon as a repetition of Thomsen's principle[164] (compare p. 324), but its accuracy was also attacked. Berthelot defended it on both grounds, but still he was not able to prove the general accuracy of the principle.[165]

It may be further remarked here, in passing, that the term thermal effect (Wärmetönung), and the words exothermic and endothermic as applied to reactions were introduced by Thomsen[166] and by Berthelot[167] respectively.

Endeavours to discover the relations between electrical and chemical forces have occupied the attention of the most talented investigators since Davy and Berzelius, without, as yet, throwing full light upon this important department. Faraday's electrolytic law[168] is an empirical one. It may today be looked upon as one of the most powerful supports of the theory of valency,[169] and still a clear theoretical apprehension of it has not yet been obtained. Even the phenomenon of electrolysis itself remains a riddle still unsolved, although various explanations have been furnished by the fine investigations of Daniell and Miller,[170] of Hittorf,[171] and of Kohlrausch.[172] One fundamental point, nevertheless, appears to have been settled. I refer to the application of the law of the conversation of energy to electrolytic processes; and to the connection between chemical energy and electro-motive force. The elucidation of these relations is due to the investigations of Braun[173] and of Helmholtz.[174] The former showed that there are galvanic elements whose electro-motive force is less, and also those whose electro-motive force is greater, than that corresponding to the chemical transformation of energy. Helmholtz established the principle that the energy of the current is equal to the chemical energy only when the electro-motive force of the battery is independent of the temperature. When the electro-motive force increases with rise of temperature, heat as well as chemical energy is used up in the production of the current; while in the converse case a part of the chemical energy is liberated in the form of heat.

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[164] Thomsen, Berichte. **6**, 423; Berthelot, Bull. Soc. Chim. [2] **19**, 485; Ostwald, Allgemeine Chemie. **2**, 20.

[165] Compare Rathke, Ueber die Principien der Thermochemie, Halle 1881; and especially Helmholtz, Zur Thermodynamik chemischer Vorgänge, Berlin. Akad. Ber. 1882, 22, 825.

[166] Pogg. Ann. **88**, 351.

[167] Mécan. Chim. **2**, 18.

[168] Phil. Trans. 1834, 77; Pogg. Ann. **33**, 301.

[169] Ladenburg, Berichte. **5**, 753.

The accuracy of this principle, besides having been proved experimentally by Helmholtz himself, has also been proved experimentally by several other investigators,[175] especially by Jahn.[176]

The relations between optical and chemical properties, which are equally important in theory and in practice, can only be touched upon here, as there are but few results of general importance to be brought forward. The chemical effects of light have been closely studied, especially in three cases:—1, That of the silver salts;[177] 2, That of the process of assimilation by the green parts of plants ;[178] and 3, That of the mixture of chlorine and hydrogen.[179]

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[170] Pogg. Ann. Ergänzungsband **1**, 565; **64**, 18.

[171] Ibid. **89**, 176; **98**, 1; **103**, 1; **106**, 337, 513.

[172] Wiedem. Ann. **6**, 1, 145.

[173] Ibid. **5**, 182; **16**, 561; **17**, 593.

[174] Berlin. Akad. Ber. 1882, 22, 825. Gesammelte Abhandlungen. **2**, 985.

[175] Czapski, Wiedem. Ann. **21**, 209; Gockel, ibid. **24**, 618.

[176] Jahn, ibid. **28**, 21.

[177] Scheele, Chemische Abhandlung von der Luft und dem Feuer, Ostwald's Klassiker, **58**, 48 *et seq.*; Senebier, Mémoires phys. chim.; Draper, Phil. Mag. [3] **19**, 195; etc.

Draper endeavoured to prove that the chemical effect produced is proportional to the intensity of the light ; and the proof was completed by Bunsen and Roscoe. It had already been recognised by Scheele that all the rays do not participate alike in the action of the light. This was confirmed by the various subsequent investigators, and it was still more definitely settled by Bunsen and Roscoe. As the principal action was repeatedly found to take place in the violet rays, the idea of specific chemical rays arose ; but this is now entirely dropped. It may be looked upon as established that rays of every wave-length can bring about chemical effects, although not with the same intensity ; and the effects vary according to the chemical nature of the sensitive substance concerned. It is further of importance that the maximum effect in different chemical processes has been found at different parts of the spectrum. It is remarkable that the numerous experiments designed to ascertain the maximum effect of the different parts of the spectrum in the process of assimilation in plants have not led to uniform results. Some find this maximum in the yellow, and others in the red. The question is one of considerable importance.

The fact recognised by Ingenhousz that the decomposition of carbonic anhydride takes place in the green parts of plants, soon led to the supposition that a connection existed between the chlorophyll colouring matter and the chemical process of assimilation ; and Dumas, as early as 1844, stated the view that the violet rays, which are the principal ones absorbed by that colouring matter, must be the most active in effecting assimilation.[180] Lommel, on the other hand, advocated the opinion,[181] that the rays lying between the lines B and C, of Fraunhofer, might play the chief part in assimilation, because they possess the greatest intensity, and also because they correspond to a maximum of absorption by chlorophyll.

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[178] Senebier, *loc. cit.;* Ingenhousz, Versuche mit Pflanzen, Leipzig 1780 ; Daubeny, Phil. Trans. 1836, 149 ; Draper Phil. Mag. [3] **23**, 161 ; Sachs, Bot. Zeitung 1864, 59 ; Müller, Bot. Untersuchungen 1872 ; Pfeffer, Pogg. Ann. **148**, 86 ; Pringsheim, Berlin. Akad. Ber. 1881, 504 ; Engelmann, Bot. Zeitung 1882, 663 ; 1883, 1, 17 ; 1884, 81, 97 ; Reinke, Bot. Zeitschr. 1884, 1 ; etc.

[179] Bunsen and Roscoe, Pogg. Ann. **100**, 43 ; **101**, 254 ; **117**, 529 ; Ergänzungsband **5**, 177.

Since the facts actually observed were not favourable to either of these views, Pringsheim, in connection with his investigations into the effect which light exercises upon the processes of oxidation within the plant organism, advanced the hypothesis and endeavoured to establish it, that the chlorophyll colouring matter is not the chemically active substance, but that it merely serves as a screen in moderating the breathing in the plant which would otherwise become excessive.[182]

Draper endeavoured to prove that, during its action, the light must be absorbed (*loc. cit.*, Note 173). Bunsen and Roscoe instituted quantitative experiments on this point, from which it appears that, in the case of chlorine and hydrogen, about one-third of the rays absorbed are used up in effecting chemical work. But there are two kinds of cases which must be distinguished : namely, those in which the light must supply the energy necessary for the chemical process (which proceeds with absorption of heat), as in the case of the assimilation by the green parts of plants, and those in which the chemical process takes place with the evolution of heat, as in the case of chlorine and hydrogen. The light appears, however, to do work in both cases, although, in the latter case, it is merely preparatory work, by which the obstacles to combination are overcome. For this effect a certain time is required, and Bunsen and Roscoe proposed to indicate this by the term photo-chemical induction.

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[180] Essai de statique chimique des êtres organisés, 24.

[181] Pogg. Ann. 143, 581.

[182] Lichtwirkung und Chlorophyllfunction in der Pflanze. 1879.

Finally, there still remains a large department to be dealt with, namely, that of molecular physics. This department has to do with the determination of the physical constants of chemical substances, and with seeking the relations between these and the chemical composition and constitution. Hermann Kopp may be looked upon as the founder of this branch of science. From the year 1842 onwards, he occupied himself with the determination of the boiling points and of the specific or molecular volumes of liquids.[183] In order that the numbers obtained might be compared with one another, they had to be determined under comparable conditions—the boiling-points under the same pressure, and all the specific volumes at the boiling-points, so that the corresponding vapours should be under the same pressure. The guiding idea in the comparison was that the same difference in composition corresponds to the same variation in the property under investigation, or that the particular property of a compound is the sum of the properties of its elementary constituents. The values pertaining to the atoms of the elements, with respect to this property, were calculated empirically, and, by means of these numbers and of the composition, the theoretical value of the property was determined for the compound. This value was then compared with that obtained by observation. Investigations of this kind were carried out in the case of molecular volumes, in particular, and harmonious results were frequently obtained. Deviations were afterwards observed, however, and it proved necessary to take the constitutions of the compounds into consideration also ; so that the value for the atomic volume pertaining to an atom was assumed to be different according to the way in which the atom was combined. A means was thus furnished, in certain cases, of checking the constitution which had been deduced, in the first place, by chemical methods only. (Compare p. 252.)

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[183] Annalen. **41**, 86, 169; **50**, 71; Pogg. Ann. **63**, 283; Annalen. **94**, 257; **95**, 121, 307; **96**, 1, 153, 303; Supplementband **5**, 323, etc.

This branch, which was investigated by Kopp with great skill and success, was then followed up further by many investigators. Researches into molecular volumes continue up to the present day, and the results obtained are discussed and turned to account in the same way that they were by Kopp.[184] But other properties of substances were also examined, and were considered in the same way in connection with composition and constitution.

This was the case especially as regards the refraction of light by liquids and gases. Since the refractive index of a substance is dependent upon the wave-length of the light as well as upon the temperature, it is not itself employed for the purpose of comparison. It is true that an endeavour was at first made to render the refractive indices independent of dispersion, by adopting as basis those for a particular wave-length. Thus Landolt at first employed, in his investigations, the indices for the C line of incandescent hydrogen. Brühl, on the other hand, employing Cauchy's formula, and after determining the refractive index for several wave-lengths, calculated a coefficient which was independent of wave-length and held for waves of infinite length.[185]

The next endeavour was directed towards obtaining results independent of the temperature, by employing, for the refractive power, the expression discovered by Laplace[186]—$\frac{n_2 - 1}{d}$ [n = refractive index, d = density]. It soon appeared, however, that this does not satisfy the required condition of being independent of temperature; and besides, on the abandonment of the emission theory of light, it had lost all physical importance. Gladstone and Dale[187] now showed empirically that the expression $\frac{n-1}{d}$ fulfilled this condition, in many cases at least. Landolt adopts the product of this value and the molecular weight (*i.e.*, the refraction equivalent) as the basis of his extensive investigations,[188] and finds that it is dependent on the constitution (the influence of chemical constitution is ascertained, but is not followed up). He thus succeeds in calculating the refraction equivalents of the elementary atoms of carbon, hydrogen, and oxygen, and in deducing from these, again, the values pertaining to the individual compounds. These frequently showed close agreement with the observed values. Landolt, however, confined his observations to the fatty organic compounds. These observations were further extended, first by Haagen,[189] and then by Gladstone,[190] who determined the refraction of many inorganic compounds and the refraction equivalents of almost all the elements.

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[184] Compare, amongst others, Pierre, Annalen. **56**, 139; **64**, 158; **80**, 125; **92**, 6; Buff, ibid. Supplementband **4**, 129; Ramsay, Berichte. **12**, 1024; Thorpe, Journ. Chem. Soc. **37**, 141, 327; Lossen, Annalen. **214**, 138; Elsässer, ibid. **218**, 302; R. Schiff, ibid. **220**, 71, etc.

[185] Annalen. **200**, 166. In a subsequent paper (Annalen. **235**, 1) Brühl discards the refraction coefficient derived from Cauchy's formula and readopts the former one.

[186] Mécanique céleste. **4**, 232.

In the meantime another value, $\frac{n^2-1}{(n^2+2)d}$, was theoretically deduced as refraction constant by H. A. Lorentz[191] and by L. Lorenz[192] in two ways that were independent of each other; and this value was employed especially by Landolt[193] and by his pupil Brühl. They give the name molecular refraction to the product obtained by multiplying this value by the molecular weight; and Brühl investigated this property in the cases of strongly refracting substances, and of aromatic compounds in particular.[194] He arrives at the conclusion that the atomic refraction of multivalent elements is variable, and that that of carbon, for instance, is distinctly greater when double or triple carbon linkings (or unsaturated carbon valencies, as he calls them) occur in the compound. He determines the amount of the increase for one ethylene linking and for one acetylene linking, and then again calculates the molecular refractions; and in this way he frequently arrives at numbers which coincide with the observed values. Later investigations of Nasini and Bernheimer[195] and of Kanonnikoff[196] have only partially confirmed the conclusions of Brühl; but the latter still hopes to be able to get rid of the exceptions.[197] J. Thomsen has shown, however, that many of the values found by Brühl can also be calculated without the assumption of double or triple carbon linking.[198] These investigations attain a special importance from the fact that, according to the conclusions of Exner,[199] the molecular refractions furnish, at the same time, the "true molecular volumes."

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[187] Phil. Trans. 1858, 887; 1863, 317. [188] Pogg. Ann. **117**, 353; **122** 545; **123**, 595. [189] Ibid. **131**, 117. [190] Proc. Roy. Soc. **16**, 439; **18**, 49; **31**, 327. [191] Wiedem. Ann. **9**, 641. [192] Ibid. **11**, 70. [193] Berichte. **15**, 1031. [194] Annalen. **200**, 139; **203**, 1, 255, 363; **211**, 121, 371.

I cannot here enter more particularly into a discussion of other investigations which are designed to show, in a similar manner, a connection between physical and chemical properties; and I shall content myself by drawing attention to individual ones. Thus there are the investigations which demonstrate a relation between the lowering of the freezing points of solutions and the molecular weights of the substances in solution (Coppet[200] and Raoult[201]), and which are connected with similar earlier experiments;[202] the research of G. Wiedemann on molecular magnetism;[203] and the investigations on the transpiration of gases by Graham,[204] by O. E. Meyer,[205] and by Maxwell,[206] and on the transpiration of vapours by Lothar Meyer.[207] There still remain to be mentioned, the fundamental investigations of Biot upon the rotation of the plane of polarisation,[208] and the researches connected with them, by Landolt[209] and others; and also the experiments of Perkin on the electro-magnetic rotation of the plane of polarisation.[210]

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[195] Beiblätter zu Wiedem. Ann. **7**, 528; Accad. dei Lincei [3] **18**, **19**, etc.

[196] Berichte. **14**, 1697; **16**, 3047; J. pr. Chem. [2] **31**, 321; **32**, 497.

[197] Annalen. **235**, 1.

[198] Berichte. **19**, 2837.

[199] Monatshefte, **6**, 249.

[200] Ann. Chim. [4] **23**, 366; **25**, 502; **26**, 98.

[201] Comptes Rendus. **94**, 1517; **95**, 187, 1030; Ann. Chim. [5] **28**, 133; [6] **2**, 99, 115; **4**, 401; **8**, 289, 317.

[202] Blagden, Phil. Trans. 1788, 277; Rüdorff, Pogg. Ann. **114**, 63; **116**, 55; **145**, 599.

[203] Pogg. Ann. **126**, 1; **135**, 177.

[204] Phil. Trans. 1846, 573; 1849, 349.

[205] Pogg. Ann. **125**, 586; **127**, 253, 353.

[206] Phil. Trans. 1866, 249.

[207] Wiedem. Ann. **7**, 497; **13**, 1.

Finally, I must refer in a few words to relations which have been discovered between crystalline form and chemical composition, a consequence of which may be a considerable expansion of the idea of isomorphism. The credit of having discovered these relations belongs to Groth;[211] and his views have been extensively confirmed by means of the numerous researches by himself and his pupils. Groth follows out the changes of the axial ratios which take place upon the entrance of substituting groups, and in this way arrives at definite laws. He gave the name morphotropy to the phenomena, and caused experiments to be made in order to determine the morphotropic influence of definite substitutions. The morphotropic effect of chlorine, bromine, and iodine, for example, proved to be analogous to that of hydrogen; and hence these elements have been designated isomorphotropic.[212] It was then announced by Hintze[213] that isomorphism might be regarded as a special case of morphotropy; a point to which Groth had, however, already directed attention.

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[208] Ann. Chim. [3] **59**, 206.

[209] Das optische Drehungsvermögen organischer Substanzen, 1879.

[210] J. pr. Chem. [2] **31**, 481; **32**, 523.

[211] Pogg. Ann. **141**, 31; Berichte. **3**, 449; compare, however, Laurent, Comptes Rendus. **15**, 350; **20**, 357; Méthode de chimie. 156; **E.** 129.

[212] Hintze, Pogg. Ann. Ergänzungsband **6**, 195.

[213] Habilitationsschrift. Bonn 1884.

LECTURE XVI.

THE DOCTRINE OF PHASES—VAN DER WAALS'S EQUATION—THEORY OF SOLUTION — ELECTROLYTIC DISSOCIATION — ELECTRO-CHEMISTRY —ATTAINMENT OF HIGH TEMPERATURES—LOW TEMPERATURES—THE NEW ELEMENTS IN THE ATMOSPHERE—THE CHEMISTRY OF NITROGEN — TRANSITION TEMPERATURE — STEREO-CHEMISTRY—RACEMISM—SYNTHESES IN THE SUGAR AND URIC ACID GROUPS —IODOSO-COMPOUNDS—TERPENES AND PERFUMES—NEW NOMENCLATURE.

WHEN we look back upon the development of chemistry during the last fifteen or twenty years, we find that it is distinguished by the constantly increasing prominence of physical or, as many call it, general chemistry, which from small beginnings has advanced to the position of a science of the first rank. Contributions to this end have, naturally, been made in particular by eminent scientists, such as Horstmann, Gibbs, van der Waals, and van 't Hoff, who have devoted themselves to this department exclusively and, by their ideas and discoveries, have brought about its advancement. On the other hand, however, it cannot be denied that this advancement does not coincide fortuitously with the appearance of Ostwald's great Text-book of General Chemistry, but that the latter, in which the attempt is for the first time successfully made to give a complete representation of what has been accomplished up to the present in this department, aroused and stimulated the tendency towards investigation in an altogether exceptional manner. Further, the establishment by Ostwald and van 't Hoff of the *Zeitschrift für Physikalische Chemie*, in which all the more important investigators in this department are active as collaborators, has done a great deal to advance the subject; so that this publication must be placed side by side with the best journals representing our science and be looked upon as of equal value with them.

In now passing on to the subject itself, I begin, in the first place, with the law of mass action, already mentioned on p. 315, which is apparently destined to play a constantly increasing part. Some of the numerous applications of the law of mass action which have been made, may be mentioned here.

The investigation by Hautefeuille,[1] and the later and more extended investigation by Lemoine,[2] into the formation of hydriodic acid from its constituent elements, aroused much interest. Lemoine believed he had verified the fact that the temperature of decomposition of hydriodic acid was influenced by pressure—a fact which would have been in contradiction to theory. Consequently, at the instigation of V. Meyer, the experiments were resumed by Bodenstein.[3] The latter found, in the first instance, a still more considerable deviation from the theory regarding the non-dependence of the equilibrium upon the pressure; and it was only in a later investigation,[4] when the source of the earlier error had been recognised and avoided, that complete agreement between experiment and theory was established.

The dissociation of gases presented frequent opportunities for the application of the theory, as, for example, in the breaking up of N_2O_4,[5] the decomposition of the compound formed by the action of hydrochloric acid gas on methyl ether,[6] the dissociation of carbonic anhydride into oxygen and carbonic oxide,[7] and so on.

The law of mass action has also been turned frequently to account in the investigations connected with electrolytic dissociation; but I shall not here enter upon the consideration of the latter subject because it is treated of separately further on.

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[1] Comptes Rendus. **64**, 608.
[2] Ann. Chim. [5] **12**, 145.
[3] Z. physik. Chem. **13**, 56.
[4] Ibid. **22**, 1.
[5] Natanson, Wiedem. Ann. **24**, 454; **27**, 606.
[6] Friedel, Bull. Soc. Chim. [2] **24**, 241.
[7] Z. physik. Chem. **2**, 782.

On the other hand, some other investigations relating to chemical equilibrium will be dealt with more particularly here.

These chemical studies received a new direction and a fresh stimulus from the theory of phases, due to Gibbs.[8] The phase rule developed by him, and proved both by him and afterwards by van der Waals,[9] is to the following effect:—Complete equilibrium can only exist when the number of phases present exceeds the number of components by one.

By phases, are understood homogeneous portions of a system. Each state of aggregation represents at least one phase. In the solid or the liquid state, two or more different phases may exist; a gas, however complex, can only form one phase.

By components are understood all those chemical elements taking part in the equilibrium, whose quantities are subject to independent variation.[10] Ammonium chloride, for example, has only one component, it being a matter of indifference whether we choose nitrogen, hydrogen, or chlorine. If excess of ammonia or of hydrochloric acid is added, there are then two independent components. Calcium carbonate, above its dissociation temperature, has two independent components, calcium and carbon; for the composition of the solid phases—calcium carbonate and calcium oxide—cannot be determined by the amount of calcium alone. Hence complete heterogeneous equilibrium is established in the case of ammonium chloride with two phases, and in the case of calcium carbonate with three phases.

Complete equilibrium is a condition which depends only on the temperature, and is mostly definable by a certain value of the pressure.

If there are $n+2$ phases and only n components, equilibrium is only possible at singular points; that is to say, at some definite temperature (multiple point, transition or transformation temperature). If there are just as many phases as there are components, the equilibrium is incomplete; that is, to each temperature there corresponds a series of pressures.

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[8] Trans. Connecticut Acad. 3, 108 and 343 (1876); German translation by W. Ostwald, Leipzig 1892.

[9] Rec. Trav. Chim. 6, 265, communicated by Roozeboom.

[10] I follow here the exposition by Planck (see Article Thermochemie, in Ladenburg's Handwörterbuch der Chemie. 11, 636).

This phase rule has found numerous applications, as the work of Roozeboom,[11] in particular, shows. Roozeboom studied the connection of the states of aggregation, the equilibrium between water and sulphurous anhydride, the hydrates of ferric chloride, etc. The phase rule can also be applied to dissociation phenomena, to the reciprocal transformation of allotropic modifications of elements, and so forth.[12]

More important perhaps than the phase rule (the significance of which is exaggerated by many) are van der Waals's theories of corresponding conditions,[13] and van 't Hoff's theory of solution.[14]

Van der Waals makes a distinct advance by substituting for the gas equation,

$$p\,v = R\,T,$$

deduced from the laws of Boyle-Mariotte and of Henry-Gay-Lussac, the expression,

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\,T,$$

in which a and b are constants which depend upon the cohesion of the gases and the not altogether negligible volume of the molecules. (According to van der Waals b is to be considered as representing four times the volume of the molecules.)

This equation not only represents the behaviour of gases (and especially of compressed gases) much more satisfactorily than the original equation, but it is also capable of application to liquids. Moreover, since the constants *a* and *b* can be determined in a simple manner from the critical data (volume, pressure, and temperature) or from the behaviour of the gases under high pressure, van der Waals's equation furnishes a mode of giving expression to the entire behaviour of all homogeneous liquid and gaseous substances with respect to changes of pressure, temperature, and volume; and, on this account, it may be regarded as of fundamental significance. Its accuracy has been proved by Young[15] in particular.

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[11] Z. physik. Chem. **2**, 449, 513; **4**, 31; **5**, 198; **10**, 477; Rec. Trav. Chim. **4** *et seq.* [12] Compare the summaries by Meyerhoffer, Leipzig 1893, and by Bancroft, Ithaca, New York, 1897. [13] Die Continuität des gasformigen und flüssigen Zustandes, Leipzig 1881. [14] Lois de l'equilibre chimique dans l'état diloué ou dissous. Stockholm 1886. Abstracted, Z. physik. Chem. **1**, 481.

The theory of solution is based upon conceptions that have arisen from the well-known experiments of Pfeffer,[16] which latter only became possible after the discovery by Traube[17] of semipermeable membranes.

In explaining osmotic pressure as the result of the impacts of the dissolved molecules upon the walls of the vessel, van 't Hoff arrives at a comparison between substances in the dissolved condition and in the state of gas. The laws of Boyle-Mariotte, and of Henry-Gay-Lussac, as well as the fundamental hypothesis of Avogadro, can now be applied directly to solutions; so that this branch, which has hitherto been one of the most obscure in the whole subject of chemistry, at once becomes fully accessible to investigation. As a consequence, important results, which are capable of being turned to account throughout the whole range of chemistry, are immediately obtained.

The important relations subsisting between the depression of freezing point, the diminution of vapour pressure, and the elevation of boiling point on the one hand, and the molecular weight of the dissolved substance on the other (which were ascertained experimentally and formulated by Raoult[18] in particular), now attain their theoretical significance for the first time. As the outcome of this, and also in consequence of improvements and simplifications that Raoult's methods of molecular weight determination underwent,[19] these methods very soon obtained a footing; and their results, especially those from the depression of the freezing point, are considered to be just as accurate as those from the vapour density.

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[15] Phil. Mag. [5] **33**, 153; **34**, 505.

[16] Osmotische Untersuchungen, Leipzig, 1877.

[17] Archiv. f. Anat. u. Phys. 1867, 87.

[18] Ann. Chim. [6] **2**, 66, 99; **8**, 289, 317; **20**, 297; Comptes Rendus. **87**, 167; Z. physik. Chem. **9**, 343, etc. The literature of the predecessors of Raoult is very fully given in Ostwald's Lehrbuch der Allgemeinen Chemie, Second Edition, **1**, 705 and 741.

Raoult had already pointed out, however, that aqueous solutions of salts, of bases, and of acids, in particular, did not agree with his rules; but always yielded results that were too low, and only attained to a value from one half to one-third of that which had to be regarded as the normal number. All explanation of this anomaly was at first wanting, so that the general applicability of van 't Hoff's theory appeared to be placed in doubt. The difficulty was got rid of in the same way as in the case of the abnormal vapour densities (compare p. 304).

Arrhenius dealt with this matter by exactly the same method that Cannizzaro, Kekulé, and Kopp had adopted in solving the other difficulty. His theory, advanced in 1887,[20] adopts as actually existent that condition which must be assumed to exist in order to arrive at an agreement between the theory of van 't Hoff and the numbers furnished by Raoult's rules. He draws attention to the fact that it is in the cases of solutions of those substances which are electrolytes and break up, under the influence of the electrical current, into their ions, that numbers are obtained which do not agree with theory. He now assumes that the ionisation does not merely take place as a result of the passage of the current, but that it occurs during the dissolution; and that the latter is thus accompanied by a more or less complete (electrolytic) dissociation, the extent of which depends principally upon the degree of dilution. A number of methods for determining the extent of this dissociation very soon presented themselves, as was pointed out by Arrhenius himself,[21] and also by Planck,[22] Ostwald,[23] and others; and (what is very important) these methods give results that agree with one another.

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[19] Compare especially, Beckmann, Z. physik. Chem. **2**, 638; **4**, 532; **8**, 223; **18**, 473, etc. [20] Z. physik. Chem. **1**, 631. Clausis (Pogg. Ann. **101**, 338) and Helmholtz (Weidem. Ann. **11**, 737) must be mentioned as predecessors of Arrhenius. Planck (Z. physik. Chem. **1**, 577) also clearly stated the idea of the dissociation of salts in aqueous solution simultaneously with Arrhenius.

The hypothesis of Arrhenius found a great many opponents—indeed it could hardly have been expected that it would be otherwise. The assumption that an aqueous solution of common salt contains free sodium and chlorine ions (which, however, are nothing but electrically charged atoms that behave like free molecules) was certain to meet with opposition from chemists, since it stood in contradiction to observation and thus included something of a metaphysical nature. Besides, the explanation of many reactions that had formerly appeared simple was rendered much more difficult; as, for example, the decomposition of water by the alkali metals,[24] since in this reaction no combination with oxygen and, on the other hand, no displacement of hydrogen ions by sodium ions could be assumed. But of what consequence are considerations of this kind in face of the great advantages which the theory of electrolytic dissociation affords? A large number of otherwise inexplicable facts are satisfactorily explained by means of it. The so-called law of thermo-neutrality, of Hess,[25] which has been confirmed, in part at least, by the well-known investigations of Thomsen[26] and of Berthelot,[27] is in complete accord with the ionisation theory, and so are the exceptions to this law which must necessarily exist in cases of incomplete dissociation ; whereas, without this theory the facts concerned constitute an incomprehensible puzzle.[28]

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[21] Z. physik. Chem. **2**, 491. [22] Wiedem. Ann. **34**, 139. [23] Z. physik. Chem. **2**, 36 and 270. [24] Compare however Ostwald, Lehrbuch. Second Edition, **2**, 989. [25] Pogg. Ann. **52**, 97. [26] Thermochemische Untersuchungen. **1**, 63. [27] Ann. Chim. [5] **6**, 325.

It is similar with the identity of the heat of neutralisation of one and the same acid by means of different bases, and of that of one and the same base by means of different acids ; also with the law of Oudemans[29] and Landolt[30] (in accordance with which the salts of optically active alkaloids and of optically active acids exhibit the same rotation in solutions of equivalent concentration), with the magnetic rotatory power,[31] and with the atomic magnetism.[32] Further, the principle in accordance with which the spectra of dilute solutions of different salts with similarly coloured ions are identical,[33] and that according to which the molecular refractive power of the salts present in aqueous solution is an additive property,[34] are explained in the same way. But probably the most important fact of this kind is that of the proportionality that exists between electrolytic conductivity and avidity in the case of acids,[35] with which may be coupled the proof, furnished by Arrhenius,[36] that the extent of the dissociation calculated from the electrolytic conductivity leads to very nearly the same results as that calculated from the depression of the freezing point. In these circumstances we cannot be in doubt as to whether the hypothesis of Arrhenius is warranted.

This ionisation theory, as it is now commonly called, leads us directly to electro-chemistry, which has made advances that were undreamt of twenty years ago, and has now developed into a separate branch of science that constantly leads to new scientific and practical results. The enthusiasm with which the discovery of the galvanic current and of the voltaic pile was welcomed, as sketched in Lecture

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[28] Compare L. Meyer, Z. physik. Chem. **1**, 134.

[29] Wiedem. Beibl. **9**, 635.

[30] Berichte, **6**, 1073.

[31] Jahn, Wiedem. Ann. **43**, 280.

[32] E. Wiedemann, in Ladenburg's Handwörterbuch. **7**, 31.

[33] Ostwald, Z. physik. Chem. **9**, 579.

[34] Gladstone, Proc. Roy. Soc. **16**, 439 ; Kanonnikof, J. pr. Chem. [2] **31**, 339.

[35] Arrhenius, Bihang Svensk. Handlingar, **8**, No. 13, 1884 ; Ostwald, J. pr. Chem. [2] **30**, 93.

[36] Z. physik. Chem. **1**, 631 ; **2**, 491.

V., was, as we now know, perfectly justified. And even although disillusionment followed the great discoveries of Ritter, Davy, Berzelius, and Faraday, and although this branch remained unproductive for decades, still the opinion has been verified of those who believed that untold treasures lay here which should one day be disclosed.

The modern subject of electro-chemistry forms a continuation to those older discoveries, and to the important investigations of Hittorf and of Kohlrausch (already mentioned on p. 326) which were now for the first time fully understood; and it leads to successive new discoveries.

In this connection, accumulators may first of all be mentioned here, since they have come into very general use, and without them it would scarcely be possible to employ electricity to advantage. Their introduction is the outcome of the discovery of polarisation by Ritter,[37] and of the very exhaustive researches of Planté, which extend as far back as the year 1859.[38] Planté constructed very powerful examples of the so-called secondary batteries; and these were afterwards improved upon in important particulars by Faure.[39]

The devising by Lippmann of the capillary electrometer,[40] which depends upon the change produced in the surface tension of mercury by polarisation, is also worthy of mention.

The theory of the voltaic pile, for which we are indebted to Nernst,[41] is very important. It is founded upon the theory of diffusion, which was advanced by Nernst himself, and upon the idea of solution pressure deduced from van 't Hoff's theory of solution. Nernst also developed the theory of concentration cells in the same way, and in doing so arrived at the same conclusions that Helmholtz[42] had already reached by thermodynamical investigation.

These matters must, however, be disposed of here by merely alluding to them, since they really belong more to the domain of physics than to that of chemistry.

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[37] Voigt's Magazin. **6** (1803), 105; compare also Gautherot, Sue, Hist. du Galvanisme. **2**, 209. [38] Comptes Rendus, **49**, 402; **50**, 640; Recherches sur l'électricité, Paris 1879. [39] German Patent, 1881. [40] Pogg. Ann. **149**, 546 (1873). [41] Z. physik. Chem. **2**, 613; **4**, 129. [42] Berlin, Akad. Ber. 1877, 713.

Turning now to subjects that concern us more immediately, we shall here first consider the progress that has been made in analytical chemistry by the application of electrolysis. The subject of electrolysis is a very old one, and so early as 1800 Cruickshank predicted that it would be turned to account in this way.[43] It was qualitative analysis, however, that alone derived any benefit from it at first.[44] Magnus afterwards drew attention to the fact that quantitative analysis—that is, the separation of the metals—must be possible by means of electrolysis;[45] and experiments in the same direction were made moreover by Gibbs[46] and by Luckow.[47] Classen,[48] Miller and Kiliani,[49] Smith,[50] Vortmann,[51] and others, afterwards introduced the manifold applications of electrolysis to quantitative analysis; and Classen devised the form of apparatus by which the experiments are generally carried out. The great importance of attention to the potential difference in these experiments was first recognised by Kiliani.[52]

The applications of electrolysis to metallurgy are probably still more important. After the researches of Davy, already fully sketched (p. 70), it was especially those of Bunsen[53] (published by the latter partly alone and partly in conjunction with Matthiessen) that brought about any notable advancement. Electrolysis first found a technical application upon the discovery of electrotyping by Jacobi and Spencer in 1839, an art which depends, however, upon an observation made by De la Rive in 1836.

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[43] Nicholson's Journal (quarto), **4**, 254.

[44] Compare, amongst others, Davy, Phil. Trans. 1807, 1; 1808, 1; Becquerel, Mém. de l'Acad. **10**, 284; Fischer, Gilb. Ann. **42**, 92; Gaultier de Claubry, Journ. Pharm. Chim. [3] **17**, 125; Niklès, Jahresbericht 1862, 610; Becquerel, Ann. Chim. [2] **43**, 380.

[45] Pogg. Ann. **102**, 1.

[46] Z. anal. Chem. **3**, 334.

[47] Dingl. Polyt. Journ. **177**, 231; **178**, 42.

[48] Handbuch der Elektrolyse; Berichte. **27**, 163 and 2060.

[49] Lehrbuch der analytischen Chemie, Second Edition, Munich 1891.

[50] Journ. Amer. Chem. Soc. **16**, 93, 420; **17**, 612, 652; Elektrochem. Zeitsch. **1**, 186 and **290**, 313; Z. anorg. Chem. **4**, 96, **267**, 273; **5**, 197; **6**, 40, 43.

[51] Elektrochem. Zeitsch. **1**, 138; Monatshefte. **14**, 536.

[52] Berg-und Hüttenmännische Zeitschrift. 1883.

[53] Annalen. **82**, 137; Pogg. Ann. **91**, 619; **92**, 648; Annalen, **94**, 107, etc,

The technical production of metals by electrolysis only became possible after the discovery, in 1872, of the dynamo-electrical machine, which was employed immediately thereafter (in the North-German Refinery at Hamburg) to remove copper from solutions. Other metals, such as zinc, magnesium, lead, silver, gold, etc., were also produced electrically afterwards. An operation of especial importance was the electrolytic production of aluminium, a metal which Bunsen first prepared by this method.[54] The technical process of Heroult[55] is different, however, from that of Bunsen, inasmuch as it is not a fused double chloride of the metal that is electrolysed, but aluminium oxide.

This is the place to refer to the great scientific and practical results that Moissan obtained as the outcome of his experiments with the electric furnace.[56] Specially worthy of mention in this connection are the preparation of artificial diamonds; the production of calcium carbide (which had, however, been discovered long before by Wöhler[57]) and of many other carbides; the preparation, in a state of purity, of chromium and of other difficultly fusible metals, etc. The first preparation of carborundum, which is also frequently attributed to Moissan, is due rather to Acheson,[58] an American. Attention must be drawn to the facts that in many of these experiments electricity is only employed as a means of attaining high temperatures (3000° to 4000°), and that the results can also be obtained in other ways, since the same high temperatures can, of recent years, be reached by means of chemical reactions. An entirely new branch of thermo-industry has thus arisen, by means of which great advances have already been made, and are still to be expected, in metallurgy. Of an earlier date is the employment of the oxy-hydrogen blowpipe in the melting and working of platinum,[59] and so is the combustion of carbon and other elements (such as silicion, sulphur, phosphorus, etc.) in air or oxygen at high temperatures, for the purpose of attaining still higher temperatures; as, for example, in the blast furnace, or in the ingenious Bessemer process. The development of these methods by Goldschmidt,[60] and their application to the production of metals such as chromium, manganese, iron, and nickel, free from carbon, and of a large number of alloys, are new however.

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[54] Pogg. Ann. **92**, 648. [55] German Patent, December 1887. [56] Le Four Électrique, Paris 1897; Comptes Rendus. **115**, 1031; **116**, 218, 1429; **117**, 425, 679; **118**, 320, 501, etc. [57] Annalen. **124**, 220. [58] Compare also Schutzenberger, Comptes Rendus. **114**, 1089.

I may here recall the interesting results obtained, partly by Victor Meyer[61] and partly by Crafts,[62] by the application of the method of vapour density determination devised by the former.[63] I regard as worthy of mention the proof that the molecule of iodine, I_2, breaks up at high temperatures into single atoms[64] (compare p. 300); and also the facts that the beginning, at least, of a similar dissociation has been ascertained in the case of bromine;[65] that the molecule of arsenic, As_4, similarly splits into two; that potassium iodide even at high temperatures corresponds to the formula KI, and cuprous chloride to the formula Cu_2Cl_2, etc.

If the attainment of high temperatures has thus been of service for the purposes of our science and of technology, so likewise the endeavours, on the other hand, to obtain low temperatures have led to great advances, and to results of altogether unforeseen importance. A long time has elapsed since the discovery of the connection between the states of physical aggregation and the critical temperature. This subject has been referred to already at p. 322, at which place the results of Pictet, of Cailletet, and of Wroblewsky on the liquefaction of the so-called permanent gases are also stated. Of especial importance were the detailed investigations of Wroblewsky and Olszewsky, who first obtained quantities of oxygen and nitrogen in the liquid state, and particularly described many of their properties.[66] The mode of measuring temperatures by determining the potential of thermo-electric currents, which is now largely employed, also originated with them.[67] In the experiments that have been carried out latterly, however, on the liquefaction of air and of other gases, Pictet's method has been abandoned again, and another method has been employed which is more nearly related to that of Cailletet. But, the latter method has been converted into a dynamical or continuous one, in which adiabatic expansion of highly compressed gases has been utilised in effecting the necessary lowering of temperature. Thus Dewar,[68] in his experiments upon the production of liquid air, liquefied, by its own expansion, air which was under a pressure of 100 atmospheres and was cooled by solid carbonic anhydride; whereas the recent technical method consists in cooling exclusively by expansion, and the effect of the latter is turned to account in a very ingenious manner by the employment of a self-intensive apparatus. Linde[69] in Germany, and Hampson[70] in England almost at the same time constructed technically efficient forms of apparatus, based upon this method, for the production of liquid air.

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[59] Hare, Phil. Mag. [3] **31**, 356; further Deville and Debray, Ann. Chim. [3] **56**, 385. [60] Annalen. **301**, 19; Z. f. Elektrochemie, **4**, 494. [61] Berichte. **13**, 1010. [62] Comptes Rendus. **90**, 183; **92**, 39; Berichte. **13**, 851. [63] Berichte. **11**, 1867 and 1946; **12**, 609 and 681, etc. [64] Comptes Rendus. **90**, 183; **92**, 39; Berichte. **13**, 851. [65] Langer and Victor Meyer, Pyrochemische Untersuchungen, Braunschweig 1885.

Liquid air has not as yet, however, found any technical application upon the large scale. Nearly pure oxygen is obtained from it very cheaply, and the attempt has been made to apply it in the technology of explosives, or to the production of high temperatures, but no ultimate pronouncement can be made with respect to this. Of far greater importance are the results that liquid air has achieved in scientific investigation.

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[66] Wiedem. Ann. **20**, 243 and 860; Wien. Akad. Ber. 1885, **91** (2), 667; Monatshefte. **9**, 1067.

[67] Compare Holborn and Wien, Wiedem. Ann. **59**, 220; and Ladenburg and Krügel, Berichte. **32**, 1818.

[68] Journ. Royal Institution, 1878; 1883-1885; 1892-1899.

[69] Z. d. Vereins deutscher Ingenieure, **39**, 1157.

[70] British Patent, April 1896.

In the first place, it must be mentioned that Dewar, by its aid, has succeeded in liquefying hydrogen,[71] and in obtaining air, oxygen, and hydrogen in the solid state; and that in doing so he has achieved almost everything that can be done in this direction. Dewar is at present engaged in trying to reach still lower temperatures by the aid of liquid hydrogen boiling under low pressure, in order to approach as nearly as possible to the absolute zero.[72]

It is also noteworthy that ozone, which was obtained in the liquid state by Hautefeuille and Chappuis in 1882 by the aid of liquid ethylene,[73] can easily be prepared in an approximately pure condition by the use of liquid air, so that Troost was able to determine its boiling point[74] and Ladenburg its density.[75] The latter determination is of especial importance, since the molecular formula O_3, deduced from it, constitutes one of the most emphatic arguments in favour of the whole molecular theory; and this formula, which till then had only been supported by Soret's experiments,[76] could not be regarded as finally settled.

But the results that have been furnished by this agency with respect to the discovery of new elements are almost of greater consequence.

When Lord Rayleigh compared the relative density of atmospheric nitrogen with that of nitrogen prepared from ammonia and other nitrogen compounds, he found a difference (in the third decimal place) which could not possibly be ascribed to an experimental error.[77] He therefore resolved upon a minute investigation in order to find out the substance that was mixed with atmospheric nitrogen. This investigation he then carried out along with Ramsay, and it led to the discovery of argon, an element of which it is very difficult to obtain any compounds.[78] The molecular weight, deduced from the density, gave the number 39.92,[79] and since by Kundt's method (compare p. 300) the monatomic character of the gaseous molecules was indicated, its atomic weight would be represented by the same number. The question as to the position of this element in the periodic system is thereby rendered an extremely difficult one, since it falls near that of potassium and yet is beyond it.

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[71] Olszewski was the first, however, who prepared liquid hydrogen. Comptes Rendus. **101**, 238. [72] Proc. Roy. Soc. **64**, 227; Ann. Chim. [7] **17**, 5. [73] Comptes Rendus. **94**, 1249. [74] Ibid. **126**, 1751. [75] Berichte. **31**, 2508, 2830; **32**, 221. [76] Annalen. **138**, 45; Supplementband **5**, 148. [77] Nature, **46**, 512.

Ramsay took up the problem from a very general point of view. It appeared to him highly probable that argon was a member of a whole group of elements, of which group he hoped to find additional members associated with nitrogen. It was thus that he came to investigate, amongst other things, the gases evolved from cléveite by heating with sulphuric acid, which Hillebrandt had considered to be nitrogen,[80] and this led him to the discovery of helium. The brightest line in the spectrum of this gas, D_3 (D_1 and D_2 are the sodium lines), had been observed a long time previously by Lockyer in the spectrum of the sun's photosphere.[81] Helium, whose atomic weight 4 was deduced from the density of the gas and from the rate of propagation of sound in it, was an analogue of argon in every respect; and it was thus clear to Ramsay that there must be another element which, with atomic weight about 20, should be placed before sodium, in the same way that helium comes before lithium, and argon probably before potassium, although the atomic weight of argon has been found, in the meantime, somewhat higher than that of potassium.[82] A similar thing applies to tellurium, the atomic weight of which, according to the most recent determinations, is greater [83] than that of iodine.[84]

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[78] Rayleigh and Ramsay, Proc. Roy. Soc. **57**, 265; Z. physik. Chem. **16**, 344; Phil. Trans. 1895 (A), 187; Berthelot, Comptes Rendus. **120**, 581; **129**, 71. [79] Berichte. **31**, 3121. [80] Bull. U.S. Geological Survey, **78**, 43. [81] Nature, **53**, 319. [82] Berichte. **31**, 3111.

Ramsay now represents the further development of the subject[85] as if the investigation, carried out with his utmost energy and effort, had remained unproductive, and as if an accident only had led him on to his further discoveries. There is in reality, however, no such accident in question, for the investigation of the residue from the evaporation of liquid air was only a link in the chain which, although perhaps unknown to himself, represented the course of his ideas. In this way he discovered krypton, the molecular weight of which was ascertained in a preliminary manner to be 45, but was subsequently fixed at 82.[86] In the case of krypton, the ratio of the specific heats has also been ascertained to be 1.66, so that this gas is also a monatomic element, the position of which in the periodic system is still undetermined.

As regards other discoveries, Ramsay found, by the systematic fractionation of argon [87] (which he condensed by means of liquid air), two new elements—neon, with atomic weight 19.9, which is clearly to be placed therefore between helium and argon and before sodium; and xenon, the density of which was first found to be 65 (H = 2), but afterwards 128. The so-called metargon proved on more minute investigation to be carbonic oxide.

Even although all doubt as to the individuality and the elementary nature of these gases is not yet removed,[88] still these investigations are unquestionably amongst the most successful that have been carried out during the last twenty years. Liquid air served not merely as starting material for the investigations, but Ramsay also employed it, or at least the liquid oxygen obtained by its aid, in an ingenious manner for the purpose of separating the various new elements.

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[83] Brauner. Journ. Chem. Soc. **67**, 549; Köthner, Annalen. **319**, 1.
[84] Compare, however, Rydberg, Z. anorg. Chem. **14**, 66. [85] Berichte, **31**, 3116. [86] Z. physik. Chem. **38**, 683. The conflicting results of Ladenburg (Berlin. Akad. Ber. 1900) require explanation. [87] Berichte. **31**, 3117.
[88] Compare Brauner, Ibid. **32**, 708.

The question as to the position of these "elements" in the periodic system has been much discussed, and up to the present it is not finally solved. On the other hand, we may now say that even if our views respecting the connection between the properties of the elements and their atomic weights should be modified on account of these newly discovered facts, still the periodic law has rendered excellent service as an invaluable guide in this obscure region.

Although such unexpected discoveries were thus made, still they will not exercise any considerable influence upon chemistry as a whole, since all these elements apparently resemble argon, and probably do not enter into many compounds. Hence it may be said that these interesting investigations will probably not prove of great significance as regards their consequences, and that in this respect they will fall short of other researches which have not excited the interest of such wide circles.

I merely recall here the isolation of fluorine by Moissan in 1886,[89] and the discovery of nickel carbonyl and allied compounds by Mond in 1890,[90] and pass on to consider more particularly the investigation of the chemistry of nitrogen, which has made great advances in recent years.

The discovery of hydroxylamine, by Lossen, falls under review here, although, of course, it took place at a much earlier date (in 1865).[91] It has not been referred to previously, however, since its importance only came to be recognised gradually, a result to which Victor Meyer's researches on the oximes[92] and their stereo-isomerism[93] materially contributed.

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[89] Comptes Rendus. **103**, 202 and 256.

[90] Journ. Chem. Soc. **57**, 749; **59**, 604.

[91] Zeitschrift für Chemie. **8**, 551; Annalen, Supplementband **6**, 220; **160**, 242; **161**, 347, etc.

[92] Meyer and Janny, Berichte. **15**, 1324; Janny, Ibid. **15**, 2778; **16**, 170; Meyer, Ibid. **16**, 822; Petraczek, Ibid. **16**, 823, etc.

[93] H. Goldschmidt, Berichte. **16**, 2176; Auwers and Meyer, Ibid. **21**, 784, 3510; **22**, 537, etc.

The preparation of phenylhydrazine, by Emil Fischer,[94] also deserves mention here. It must be looked upon as of particular importance, on account of its leading to the clearing up of the sugar group.[95] Following upon this there are the valuable researches of Curtius, who discovered hydrazine in 1889,[96] and hydrazoic acid in 1890.[97] The utilisation of these two substances has already led to numerous investigations, and will lead to others. As worthy of mention, I also refer to the researches of Thiele,[98] who (amongst other things) found out a convenient and technically practicable method for the manufacture of hydrazine; and to those of Raschig,[99] who cleared up the nitrogen-sulphonic acids, and in doing so discovered the method now employed for the production of hydroxylamine.

It does not seem to me that this is the place to enter more fully into this subject, since I am really giving a historical sketch, in which only those things that are of general importance can be prominently brought forward.

I may thus recall here a discovery of Hellriegel's which marks an epoch in chemistry and agriculture.[100] According to Hellriegel, leguminous plants, and lupins in particular, possess the power of assimilating, with the aid of lower organisms, the nitrogen of the air. In this connection the fact must not be passed by without mention that Berthelot had previously asserted the assimilation of free nitrogen.[101]

An observation which is to a certain extent of an opposite character is the proof furnished by Buchner that fermentation is possible even without living organisms, by means of the liquid expressed from yeast (zymase).[102]

More particular consideration may be given to a research by van 't Hoff, in which the idea and the significance of the transition temperature are clearly stated.[103] Van 't Hoff is led to the idea by the comparison of chemical reactions with the transitions from one of the states of physical aggregation to the others; but the same conception may be arrived at by the aid of the phase rule.

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[94] Berichte. **8**, 589; compare also Strecker and Roemer, Ibid. **4**, 784; and Zeitschrift für Chemie. **14**, 481.

[95] Berichte. **17**, 579.

[96] Curtius and Jay, J. pr. Chem. [2] **39**, 27.

[97] Curtius, Berichte. **23**, 3023.

[98] Annalen. **270**, 1; **273**, 133; Berichte. **26**, 2598 and 2645, etc.

[99] Annalen. **241**, 161.

[100] Hellriegel and Wilfahrt, Biederm. Centr. **18**, 179.

[101] Comptes Rendus. **106**, 569.

[102] Berichte. **30**, 117, 1110, 2668, etc.

Since the observations of St Claire Deville (see p. 302), the phenomena of dissociation have been regarded and treated as analogous to those of evaporation. Van 't Hoff now shows that there are reactions which are comparable with the process of fusion, and in which a fixed temperature marks the line of separation between two chemically different conditions. This fixed temperature he designates the transition temperature; and he demonstrates the accuracy of his idea in the cases of the formation of double salts (astrakanite), of the preparation of elements in allotropic modifications (sulphur), and of the splitting of racemic substances (sodium ammonium racemate).

He afterwards treated this subject in a much more detailed manner in an important monograph[104] "On the Formation and Decomposition of Double Salts," in which he explains the theory of the matter, and describes the methods for experimentally determining the transition temperature.

These investigations have found very important applications in relation to the deposition of salts from ocean water,[105] and in explaining the splitting of racemic compounds by Pasteur's methods.

This leads us directly to the subject of stereo-chemistry, which has already been discussed in Lecture XIII. (see p. 268), but which has acquired so much importance of late that I must return to it here.[106]

Attention has already been called to the fact that all compounds with asymmetric carbon atoms do not possess optical activity. It was possible to show, however, that facts of this description only constitute apparent exceptions since it could be proved in very many instances that the compounds concerned are "racemic" (that is, that, like racemic acid, they can be split into their enantiomorphous constituents, or that they are mixtures of such mirror-images), or that they are meso-compounds (that is, that they behave like meso-tartaric acid, which, it is true, is only possible in the case of substances with symmetrical structural formulæ).

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[103] Van 't Hoff and Deventer, Berichte. 19, 2142.

[104] German Edition by Dr Paul, Leipzig 1897.

[105] Berlin. Akad. Ber. 1897, 1898, 1899, 1900, 1901, 1902.

[106] Compare van 't Hoff: Die Lagerung der Atome im Raume, Second Edition, Braunschweig 1894.

The theory of the asymmetric carbon atom was tested, in the first instance, in isolated cases only, and, amongst others, in the splitting by means of fungi of a series of alcohols, which Le Bel succeeded in effecting;[107] and in the splitting of synthetic coniine,[108] which was of importance inasmuch as it was the preparation, for the first time, of an active base. The theory was subjected to a systematic examination by Emil Fischer, in carrying out his well-known syntheses in the sugar group.[109]

It is simply astonishing that the theory stood the test of this *experimentum crucis*, and that the sagacity of Fischer enabled him to fix the configurations of the individual hexoses[110] without encountering any contradictions in doing so, especially when we take into consideration the recent experiments of Walden,[111] in accordance with which it is possible, by means of simple chemical reactions, to pass at ordinary temperatures from an active substance to its enantiomorph.

As regards the application of the theory of asymmetric carbon atoms to molecules with doubly linked carbon atoms,—a matter that van 't Hoff had already mentioned, but one which had met with less attention,—very special notice was called to it by Wislicenus,[112] who, moreover, had himself given the first impulse to stereo-chemical conceptions by his earlier and extended investigations of lactic acid.[113]

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[107] Comptes Rendus. **87**, 213; **89**, 312; Bull. Soc. Chim. [3] **7**, 551; Comptes Rendus. **92**, 532. [108] Ladenburg, Berichte. **19**, 2578; Annalen. **247**, 83. [109] Berichte. **23**, 2114; **27**, 3189. [110] Ibid. **24**, 1836 and 2683. [111] Berichte. **28**, 2766; **29**, 133; **30**, 2795 and 3146.

The researches of Wislicenus and his pupils[114] have certainly supplied most valuable contributions towards the clearing up of these remarkable cases of isomerism—an end towards which (after the discovery of fumaric[115] and maleic[116] acids) a great many chemists, and even Kekulé himself,[117] had aspired in vain. In this domain, however, there are still many unexplained contradictions, as Michael[118] and Anschütz[119] in particular have shown. On the other hand it must be admitted, that by van 't Hoff's theory an extremely plausible explanation of the products arising from the oxidation of fumaric and of maleic acids is rendered possible.[120]

The applications of the doctrine of asymmetric carbon atoms to substances containing rings are also important and interesting. The first principles were laid down by van 't Hoff;[121] but their significance was only fully recognised when Baeyer published his extended investigations upon hydrogenised aromatic compounds, and, in particular, upon the hydrophthalic acids.[122]

While Baeyer's intention in these investigations was to discover weaknesses in the theory, and even to modify it, his labours led instead to a further confirmation of it. Besides this, the credit is due to him of having advanced the so-called tension theory,[123] which has already proved of service in some cases.

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[112] Uber die räumliche Anordnung der Atome in organischen Molekulen und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen, Leipzig 1887.

[113] Annalen. **125**, 41; **128**, 1; **133**, 257; **146**, 145; **166**, 3; and especially **167**, 345.

[114] Ibid. **246**, 53; **248**, 1, 281; **250**, 224; **272**, 1; **274**, 99.

[115] Pfaff, in Berzelius' Jahresbericht 1828, 216.

[116] Pelouze, Annalen. **11**, 263.

[117] Ibid. Supplementband **2**, 111; Zeitschrift für Chemie. **10**, 654.

[118] J. pr. Chem. [2] **38**; **43**; **46**; **52**, etc.

[119] Annalen. **254**, 168.

[120] Kekulé and Anschütz, Berichte. **13**, 2150; **14**. 713.

[121] La chimie dans l'espace.

[122] Annalen. **245**, 103; **251**, 257; **256**, 1; **258**, 1 and 145; **266**, 169; **269**, 145; **276**, 255.

[123] Berichte. **18**, 2278.

Emphasis must be laid upon the fact that the important consequences which the theory of the asymmetric carbon atom brought forth, gave a spur to the more and more complete application of stereo-chemical considerations. In this connection the numerous researches may be mentioned which deal with the non-occurrence of certain reactions, and explain this on stereo-chemical grounds.[124] Amongst these investigations the best known are those of Victor Meyer on the formation of esters.[125] The asymmetry of the nitrogen atom may also be mentioned in this connection.

The researches of Hantzsch and Werner[126] were of fundamental significance with respect to the last-named subject, and they were capable of explaining the isomerism amongst oximes, which was already familiar at that time. Hantzsch afterwards extended the views respecting this matter, and turned them to account in explaining the isomeric hydrazones[127] and diazo-compounds.[128] It is true that it was only geometrical isomerism in the case of nitrogenous organic compounds that was proved by these investigations. Le Bel[129] and Ladenburg[130] endeavoured to prove that asymmetric nitrogen can further produce or influence optical activity. The investigations of both have, however, been attacked,[131] but both have been able to establish the accuracy of their results.[132] Pope and Peachey subsequently prepared optically active compounds of sulphur [133] and of tin.[134]

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[124] Hofmann, Ibid. **17**, 1915; and **18**, 1825; Jacobson, Ibid. **22**, 1219; **25**, 992; **26**, 681 and 699, etc.; Pinner, Ibid. **23**, 2917; Küster and Stallberg, Annalen. **278**, 207.

[125] Berichte. **27**, 510, 1580, 3143; **28**, Ref. 301 and 916; **29**, 830, etc.

[126] Ibid. **23**, 11; Werner, Räumliche Anordnung der Atome in stickstoffhaltigen Molekülen, 1890. Compare further, the previously published researches of Willgerodt, J. pr. Chem. **37**, 449; Burch and Marsh, Journ. Chem. Soc. **55**, 656; and especially van 't Hoff, Ansichten über die organische Chemie, Braunschweig 1878-81.

[127] Fehrlin, Berichte. **23**, 1574; Krause, Ibid. **23**, 3617; Hantzsch and Kraft, Ibid. **24**, 3511; Marckwald, Ibid. **25**, 3100.

[128] Ibid. **27**, 1702, 1726, 1857, 2099, 2968, 3527; **28**, 741, 1124, 1734, etc.

[129] Comptes Rendus. **112**, 724.

[130] Berlin. Akad. Ber. 1892, 1067; Berichte. **26**, 854; **27**, 853 and 859.

[131] Marckwald and Droste-Huelshoff, Ibid. **32**, 560; Wolffenstein, Ibid. **29**, 1956.

Another subject that was much discussed was the significance of racemism, about which a clear understanding only became possible upon the introduction of the conception of the transition temperature, and upon the recognition of the analogy between racemic substances and double salts. The most important method of splitting racemic substances—that by means of optically active substances—remained a standing enigma as long as the existence of partially racemic substances was denied.[135] Every difficulty was removed, however, after Ladenburg had shown that such substances do without doubt exist,[136] and after a transition temperature had been recognised in their case also.[137]

Furthermore, the much debated question as to how a truly racemic substance (inactive by intra-molecular compensation) can be distinguished from the mixture of the active components, may now be looked upon as practically settled.[138]

It is beyond doubt that the founding and development of stereo-chemistry (a name which originated with Victor Meyer [139]) is the most important thing that was accomplished in organic chemistry during the last two decades of the nineteenth century. Stereo-chemistry possesses a significance for this period similar to that which the foundation and introduction of the theory of aromatic compounds possessed for the twenty years preceding. There are besides, however, other important investigations in organic chemistry which require to be mentioned.

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[132] Le Bel, Comptes Rendus. **129**, 548; Ladenburg, Berichte. **29**, 2706; **34**, 3416; compare further Wedekind, Ibid. **32**, 511 and 722; Pope and Peachey, Journ. Chem. Soc. **75**, 1127; **79**, 828.

[133] Ibid. **77**, 1072.

[134] Proc. Chem. Soc. **16**, 42.

[135] E. Fischer, Berichte. **27**, 3226; Landolt, Das Optische Drehungsvermögen, Second Edition, Braunschweig, 1898, 85.

[136] Ladenburg and Herz, Berichte. **31**, 937; Ladenburg and Doctor, Ibid. **31**, 1969.

[137] Ladenburg and Doctor, Ibid. **32**, 50.

[138] Roozeboom, Z. physik. Chem. **28**, 494; Berichte. **32**, 537; Ladenburg, Journ. Chem. Soc. **75**, 465; Berichte. **32**, 864; Pope and Peachey, Journ. Chem. Soc. **75**, 1111.

[139] Berichte. **23**, 568.

A matter of general importance was the introduction of the idea of tautomerism or desmotropy, which was brought forward by Laar,[140] in 1885, on the strength of some experimental observations and remarks by Zincke.[141] Laar applies the term tautomeric to a compound when two or more structural formulæ can be advanced in explanation of its interactions. A very well-known example is furnished by aceto-acetic ether, which reacts sometimes as if it should be represented by the ketone formula $CH_3.CO.CH_2.COOC_2H_5$, and sometimes as if it should be represented by the enol formula $CH_3.C(OH):CH.COOC_2H_5$. There are numerous investigations dealing with substances of this kind, of which there are a large number. Some of the best known of these investigations are those of Claisen,[142] of W. Wislicenus,[143] and of Knorr.[144] Opinions are still widely divergent, with regard to the questions as to whether a desmotropic substance is to be considered as a mixture of two or more compounds (Laar), or whether the forms are continuously passing into one another by means of oscillations (Kekulé) or shifting linkings (Knorr[145]), or finally whether one form is stable under certain conditions while another is stable under different conditions.

The systematic and, theoretically, almost completed examination of the sugar group has already been referred to (p. 351). The uric acid group, which so long resisted elucidation and synthesis, is now completely cleared up,[146] and this is chiefly due to Emil Fischer's synthetical investigations.[147]

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[140] Berichte. **18,** 648; **19,** 730; compare also Butlerow, Annalen. **189,** 76. [141] Berichte. **17,** 3030. [142] Annalen. **291,** 25. [143] Ibid. **291,** 147. [144] Ibid. **293,** 70. [145] Ibid. **279,** 188. [146] Compare further, Grimaux, Ann. Chim. [5] **11,** 356; and **17,** 276; Horbaczewsky, Monatshefte. **3,** 796; **6,** 356; **8,** 201; Behrend and Roosen, Annalen. **251,** 235; W. Traube, Berichte. **33,** 1371 and 3035. [147] Berichte. **30,** 549, 559, 1839, 1846, 2220, 2226, 2400, 3009; **31,** 104, 431, 542, 1980, 2546, 2550, 2619, 2622; **32,** 435.

The hydrogenised aromatic compounds have likewise been referred to already (p. 354), but the terpenes have not been mentioned. The latter formerly constituted one of the most confused sections of organic chemistry, whereas Wallach has now succeeded in systematising them by his extended and careful researches.[148] But the most important thing about them, the elucidation of their constitution, is still wanting; for, in spite of some fortunate attempts by Baeyer,[149] which led to the synthesis of substances resembling terpenes, no one has yet succeeded in making this clear.

The discovery of the iodo-, iodoso-, and iodonium-compounds, for which we are indebted to Willgerodt[150] and to Victor Meyer,[151] is also important, and these compounds supply new knowledge concerning the nature of iodine. The discovery of antipyrine by Knorr[152] was of great importance in medicine, and through it the pyrazol group[153] came to be simultaneously explored.

The preparation of the so-called substantive azo-dyes has become of technical importance;[154] and of much greater consequence is the manufacture of ammonia soda, and that of synthetic indigo, according to a method discovered by Heumann.[155] The latter is probably the most striking example of the eminent service which a close union of technical practice with science is capable of rendering. The detailed history of this subject, which has now been placed at our disposal in the exposition by Brunck,[156] presents an abundance of interesting and instructive matter. In this connection it may be pointed out specially that the manufacture of synthetic indigo has brought to maturity a new method of obtaining sulphuric acid,[157] which may, perhaps, displace the old-established method. That catalytic processes have been called into requisition both in the preparation of the anthranilic acid necessary for the indigo manufacture, and in the combination of sulphurous anhydride and oxygen, has directed the attention of chemists anew to this subject, which was dealt with so frequently at an earlier period.[158]

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[148] Annalen. **225**-**320** (52 papers).

[149] Ibid. **278**, 288; Berichte. **26**, 232.

[150] J. pr. Chem. [2] **33**, 154; Berichte. **25**, 349; ; and **26**, 1802.

[151] Ibid. **25**, 2632; **26**, 1354; **27**, 1592; **28**, Ref. 80.

[152] Ibid. **17**, Ref. 148 and 149. Also Ibid. **17**, 2032, etc.

[153] Annalen. **279**, 188; **293**, 1.

[154] German Patent No. 32958, 1884.

[155] Berichte. **23**, 3043, 3431.

[156] Ibid. **33**, Sonderheft, lxxi.

[157] Ibid. **34**, 4069.

Great advances have likewise been made in the preparation of artificial perfumes. Vanilline has already been referred to. The manufacture of piperonal[159] (heliotropine), and especially the synthesis of ionone by Tiemann and Krüger,[160] must be mentioned in this connection.

This account of the most recent phases in the development of our science must not be concluded, however, without reference being made to the valuable, although unfinished, researches which were carried out under the direction of Friedel, and which aimed at the introduction of a new nomenclature into organic chemistry.[161] Although it has not yet been possible to extend the system to substances containing rings, still there is much that is good and valuable in the principles that have been advanced.

With the foregoing observations I may be permitted to conclude these lectures. I shall be gratified if the matters that have been discussed should prove to be of value in conveying an outline of the history of our science; and, in any case, I hope that the lectures may serve as a stimulus to independent study. There are few things which operate more advantageously in the latter direction than a survey of the past. We recognise that progress is only possible with the united activity of many workers; we realise that even the smallest contribution is not useless; and we are led to exercise our own small capacities in the hope that they also may increase, by a drop, the tide of general knowledge.

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[158] Ostwald. Elektrochem. Zeitsch. **7**, 995.

[159] Annalen. **152**, 25.

[160] Berichte. **26**, 2675; **28**, 1754.

[161] Compare the report by Tiemann, Berichte. **26**, 1595.

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